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A Review of Approaches to the Study

of Turbulence Modification

by Means of Non-Newtonian Additives

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ABSTRACT

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A condensed review of topics relevant to theoretical study of drag reduction by non-Newtonian additives is presented. In addition, the techniques and results of experimental investigations of this phenomenon are examined.

It is proposed that dilute solutions of polymers or surfactants can be rheologically characterized by measuring the secondary flow characteristics that occur in the neighborhood of an oscillating cylinder. Plans for conducting these measurements are presented.

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1. INTRODUCTION

Few discoveries of recent years in the area of fluid mechanics have created such intense interest and economic speculation as drag reduction. This term refers to the drastic reduction of friction drag which occurs under conditions of turbulent flow when minute amounts of an additive (usually polymer) are added to a fluid flowing at a fixed flow rate. This unusual phenomenon provides a physical means of reducing energy losses due to the turbulent skin friction in both internal and external flows.

So, drag reduction has very important technological, medical, industrial, scientific and military applications.

It has been an active area of research for many years. Many researchers have tried to explain all complex phenomena associated with drag reduction. The result of the tremendous interest on the subject has been the production of more than 1200 papers since 1948, when Toms for first time observed the phenomenon.

Although many efforts have been made in order to completely understand the phenomenon of drag reduction, basically its mechanism is still not fully explained. Remaining questions are related to the macromolecular behaviour under conditions of turbulent flow, rheological characterization of the additives, turbulent boundary layers, shear stability of the additives, investigation of new drag reducing agents, and heat and mass transfer effects.

The purpose of the research proposed here is to improve our understanding of the phenomenon. Specifically, we wish to contribute to the area of rheological characterization of dilute polymer solutions and surfactants, and to gain a better understanding of how the molecular behaviour of the additives is related to the mechanism of turbulent drag reduction.

2. LITERATURE REVIEW

2.1. Historical.

The drastic reduction in wall shear stress caused by the addition of small amounts of linear macromolecules to a flowing fluid in turbulent flow was first reported by Toms, in 1948. In his pioneering paper Toms showed that the addition of minute amounts of polymethylmethacrylate to high Reynolds number turbulent pipe flow of monochlorobenzene reduced the pressure drop substantially below that of the solvent alone, at the same flow rate (Toms,1949,1977). So, drag reduction is occasionally termed the "Toms phenomenon" or "Toms effect", in honor of Toms, or "Texas effect", in view of the contributions of Texas investigators. Since the time of Toms' observations the phenomenon had been overlooked for quite a number of years, and it was not until the late fifties that scientists started showing their interest in it.

In the early sixties the U.S.Navy became interested in the potential of drag reduction for military applications and supported research in numerous laboratories and research centers.

After more than twenty years of active research in this field many
important contributions have been made. However, even if many different
additives and the effect of many parameters involved in the phenomenon
have been investigated, drag reduction is still, as mentioned above, not
fully understood.

The results of the work done on the subject are available in a
number of reviews and reports by Kramer (1961), Shenoy (1984), Lumley
(1969,1973), Berman (1978), Virk (1975), Little et al (1975), Hoyt
(1972,1977), Palyvos (1974), Bark et al (1975), Lumley and Kubo (1984),
Patterson et al (1969), Sellin et al (1982a,1982b), Povkh (1984) and
Kubo and Lumley (1980).

2.2. Definitions.

In 1961 Savins defined drag reduction as the increase in pumpability
of a fluid, which is achieved on the addition of small amounts of
certain materials to the fluid, when it is flowing under turbulent
conditions. This definition is general and widely accepted and is
equivalent to the definition of drag reduction as the reduction of skin
friction in turbulent flow below that of the solvent alone
(Lumley,1969). However, this definition implies two restrictions:
First, that the flow be turbulent after the addition of the drag
reducing agent (e.g. polymer). Second, that the skin friction not
simply be lower than that of a Newtonian fluid having the same viscosity

as the polymer solution at the wall stress in question, but lower than that of the solvent. In symbols, drag reduction for pipe flow is given by the expression:

$$\text{Drag Reduction} = (\Delta P_s - \Delta P_a)/\Delta P_s$$

where ΔP_s is the pressure drop due to the friction in unit length of the pipe for the solvent alone, and ΔP_a is the corresponding pressure drop for the dilute solution containing the additive. The above expression is valid for constant flow rate through the pipe. An equivalent expression in terms of the friction factor is:

$$\text{Drag Reduction} = (f_a - f_s)/f_s$$

where f_a is the friction factor for the dilute solution, f_s refers to the solvent, and both are evaluated at the same Reynolds number (Ting and Little,1973; Berman,1978).

In order to measure the drag reducing ability of an additive, the Drag Ratio (DR) was introduced by Savins (1964), at constant flow rate through a pipe:

$$DR = \Delta P_a/\Delta P_s$$

A very important concept related to drag reduction is that of dilute polymer solution. According to Lumley (1969), a dilute polymer solution can be defined as a polymer solution with concentration less than a critical one. This critical concentration can be defined in terms of the effective diameter of the polymer (say the root-mean-square end-to-end distance of the polymer molecule), as the concentration at which the

polymer molecules, if they were spheres of their effective diameters, would be in dense spherical packing. That is, they would occupy 74% of the actual volume. Practically, we can have dilute solutions (approximately 100-500 wppm), very dilute (less than 100 wppm) and concentrated solutions (above 500 wppm), but this is not a strict definition. The Toms phenomenon takes place strongly in dilute solutions, although it is observed to continue as the solution becomes concentrated (i.e. with concentration greater than the critical).

Since most of the work done in the area of drag reduction is related to turbulent pipe flows, the most common way to express drag reduction is by using the friction factor versus Reynolds number plot, as shown in figure 1, at the end of this work. There are some alternative ways to represent drag reduction: For example, the flow rate versus pressure drop or wall shear stress plots (figures 2 and 3) or plots of percent drag reduction versus a relevant parameter, like concentration (figure 4). Also, the plots of drag ratio versus flow rate and the "hydraulic capacity diagrams" (flow rate versus concentration plots, with pressure drop as parameter) are frequently used (Zakin and Hunston,1980; Little,1971; Ting,1982; Palyvos,1974; Fabula,1963).

As mentioned above, this work deals with the reduction in friction drag. It should be emphasized, however, that if wave and inductive drags are neglected, then the hydraulic drag, in the general case (either internal or external flows), consists of two components, namely

the shape or pressure drag, and the friction drag. The pressure drag is a function of the shape of the body in flow, and is controlled by the pressure field on the body's surface. The friction drag is due to friction forces. Usually the drag is not estimated from the forces themselves, but from their coefficients. So, one can write:

$$C_\infty = C_{\infty fr} + C_{\infty pr}$$

where C_∞ is the drag coefficient, and the subscripts fr and pr refer to its friction and pressure components, respectively. The percentage of frictional drag in the total drag is much higher in internal than in external flows (Povkh,1984).

It is clear that all interesting features of the drag reduction phenomenon are associated with the friction drag. So, in the course of this work the term "drag reduction" refers to the reduction in friction drag.

2.3. Drag reducing additives.

According to Shenoy (1984), the additives which reduce the turbulent drag can be broadly classified under four headings:

1. Polymers

2. Solid particle suspensions.

3. Surfactants.

4. Biological additives.

2.3.1. Drag reduction by polymers.

Most of the studies on drag reduction have been undertaken with dilute solutions of soluble high-molecular weight polymers in both aqueous and organic solvents.

The most commonly used polymers are dilute solutions of polyethylene oxide (polyox) in water (Virk et al,1967) and solutions of polyacrylamide in water (Virk,1975b; Metzner and Park,1964). As reported by Fabula (1963), dilute solutions of linear polyox are the most effective drag reducers (the drag reduction can be up to 80%). This statement is still valid (Shenoy,1984).

There are many other polymers which are effective drag reducers as, for example, guar gum, polyisobutylene, xanthan gum, polystyrene, etc. The structure of some typical drag reducing polymers is shown in Table 1, in the end of this work. Among the different solvents used, the most popular are water and hydrocarbons (e.g. benzene,toluene, kerosene). Tables with the most important drag reducing polymer solutions are available in the literature (Virk,1975a; Shenoy,1984; Holtmyer and Chatterji,1980).

The advantage of using polymers as drag reducers is that they are effective at very low concentrations. As mentioned above, they can reduce the friction in turbulent flow as much as 80 percent below that exhibited by the solvent alone at the same flow rate. However, they have

a very important disadvantage, the mechanical degradation, which limits their practical applicability (Little et al,1975; Ting and Little,1973). Virk (1975a) reported that the polymer solutions degrade very fast. Their mechanical degradation in flow (flow-induced degradation) has been the subject of many theoretical and experimental studies (Little et al,1975; Odell et al,1983; Krozer,1984; Kim et al, 1986) because of its importance.

It is generally accepted that the high shear field associated with turbulence is responsible for polymer degradation. Since chemical and thermal degradations are negligibly small under ordinary conditions (Patterson and Abernathy,1970), the turbulent shear stress induces scission of molecular entanglement or of individual molecules associated with very high local shear rates. On the other hand, it was proposed by White (1970) that degradation is caused by a rapid chemical reaction initiated by turbulence. Actually, the degradation process results in a decrease in polymer molecular weight. Specifically, Patterson et al (1966) have shown that for polyisobutylene the viscosity-average molecular weight, to which the viscosity of the solution is proportional, decreased by 20 % whereas the drag reducing ability of the solution has decreased by 56 %. A gel permeation chromatography analysis of the degraded polymer showed that the higher molecular weight portion is preferentially degraded.

Ting and Little (1973) proposed a method for the laboratory

characterization of polymer degradation in turbulent pipe flow by introducing the notion of degradation index, K_d , for the polyox polymer family. Specifically, they used the normalized molecular weight, $M_R = M_w/M_0$ where M_w is the observed molecular weight of the compound and M_0 is the molecular weight before degradation. They expressed M_R as a function of the dissipated energy function,

$$E = \int_0^t \tau_w \cdot \dot{\gamma} \, dt,$$

with τ_w being the turbulent wall shear stress experienced by the polymer sample in the pipe and $\dot{\gamma}$ is the mean shear rate:

$$M_R = 1/(1+K_1 E)$$

This expression was compatible with the experimental results for the polyox polymers. The constant K_1 determines the rate of decay and is related to the initial molecular size. Then, the degradation index of the polyox family is defined as:

$$K_d = K_1/[\eta]$$

where $[\eta]$ is the intrinsic viscosity. It was found that $K_d = 0.13$ for polyox polymers. The inverse of K_d is a measure of the energy involved in degrading a unit weight of the polymer additive in the flow.

Virk et al (1966) showed that there exists a critical wall shear stress below which no degradation takes place. Actually, they found that degradation becomes severe once the wall shear stress exceeds the onset wall shear stress for drag reduction.

The complications involved with the calculations of turbulent flow

of drag reducing polymer solutions forced more scientists to concentrate on the experimental studies of polymer degradation. There exists a fairly large amount of experimental information on drag reducing flows, in which mechanical degradation takes place (Hunston and Zakin,1980; Sylvester and Kumor,1973). From these investigations we can conclude that drag reduction is directly proportional to the molecular weight of the polymer, regardless of the solvent type. Also, the nature of solvent influences the concentration of polymer required for a certain degree of drag reduction (greater concentrations required in poor solvents) and, therefore, plays an important role in polymer degradation, which is actually observed in dilute solutions. Under fixed flow conditions, more mechanical degradation is observed in a poor than in a good solvent. The shear degradation at a given shear stress is independent of the solvent's viscosity. Entanglements don't play dominant role in the degradation mechanism. The loss of drag reduction, Λ, through mechanical degradation during time t can be approximately described by the equation:

$$\Lambda/\Lambda_0 = e^{-Rt}$$

where Λ_0 is the drag reduction of fresh solution and R is a parameter. As the polymer concentration decreases, the rate of degradation increases or remains the same. The above experimental evidence led Brostow (1983) to the development of a statistical-mechanical model of chain conformations for the prediction of mechanical degradation in flow.

Berman (1978) suggested that degradation offers an alternative explanation of why drag reduction is not observed for vanishingly low concentrations, and proposed that it could play a major role in the degradation mechanism. However, even if degradation is related to the drag reduction mechanism, it was shown that drag reduction can be observed in exceptionally low concentrations. Oliver and Bakhtiyarov (1983) detected drag reduction in a simple apparatus when the polymer concentration was only 0.02 wppm.

At this point it is worthy to note that variations in the drag reducing effectiveness of the solutions made with the same polymer may occur due to variation in molecular weight distribution from batch to batch, aging, differences in mixing procedures in the preparation of the solutions, differences in waiting times from when the polymer solution was prepared and laboratory measurements were made, differences in the chemical properties (e.g. pH) and purity of the solvent (Hoyt,1972; Lee et al,1980; Schowalter,1978; Astarita and Marrucci,1974; Tanner,1985). Also, the solution temperature for the drag reduction experiments is very important (White,1969).

The effects of solvents on drag reduction of polyox solutions were studied by Kwack and coworkers (1981), who concluded that the hydrodynamic behaviour of dilute aqueous solutions of high molecular weight polymers is very sensitive to the chemistry of the water. They also suggested that mechanical degradation results in increased friction

factors. This latter effect increased with increasing concentration or increasing flow rate.

It can be concluded from the above development that, since the polymers degrade very fast and, consequently, their drag reducing ability is impaired, it is very important to develop materials which can retain their drag reducing ability for larger duration of time. One way to develop such new materials is to use mixtures of polymers instead of individual polymers. Dschagarowa and Bochossian (1977) performed experiments with solutions of polybutylene-isoprene rubber in toluene. Both polymers are good drag reducing agents, and it was found that their mixture was a good drag reducer, as well. The same authors obtained in 1978 satisfactory results for mixtures of polyisobutylene and 1,4 cis-isoprene rubber dissolved in toluene, at very low concentrations. Very recently, Reddy and Singh (1985) measured the turbulent drag reduction caused by polymer-polymer mixtures in recirculatory flow of water. They predicted the phenomenon by using simple mixing rule equations including an interaction parameter. This parameter depends upon the polymer-polymer interaction in the mixture. Actually, they used the following equations:

$$DMC_1 = DR_1 \cdot W_1 + DR_2 \cdot W_2$$

$$DMC_2 = DR_1 \cdot W_1 + DR_2 \cdot W_2 + I \cdot W_1 \cdot W_2$$

$$DMC_3 = DR_1 \cdot DR_2 \cdot (DR_1 \cdot W_2 + DR_2 \cdot W_1)$$

where DMC_1, DMC_2 and DMC_3 are drag reductions by mixtures, DR_1, DR_2 and W_1, W_2 are drag reductions by and weight fractions of components 1 and

2, respectively, in the mixture ($W_1+W_2=1$), and I is the interaction term (adjustable parameter).

They also studied the degradation of the mixtures and found that mixtures with optimum composition (which gives the maximum synergistic effects (Haken,1978) in drag reduction effectiveness) are more shear resistant. Some of the shear resistant mixtures they used were xanthan gum-guar gum, guar gum-polyacrylamide and xanthan gum-polyacrylamide.

Other interesting drag reducing mixtures are the polymer-soap mixtures. Patterson and Little (1975) showed that mixtures of polyox and carboxylate soaps can be more effective drag reducers than solutions of polyox in water.

It is important to point out that the technique of injection of polymer solutions into turbulent flow influences their drag reducing behaviour. For example, for the case of turbulent pipe flow, McComb and Rabie (1982) observed that when polymer solution was injected at the centerline of the pipe, the local drag reduction increased with distance downstream from the injection point and eventually reached an asymptotic value. This was due to the polymer spreading out radially, as the injected solution was carried downstream. When, however, the polymer solution was spread uniformly across the pipe, the local drag reduction attained its constant, asymptotic value. The value of the asymptotic drag reduction obtained in the former method was greater than that obtained in the latter one. Similar experimental studies have been made

recently by Walker et al (1986) who tried to optimize the injection process for the drag reducing solutions. Notice that the drag reduction obtained by injecting a polymer solution thread into the center of a turbulent pipe flow is called non-homogeneous drag reduction, and has been the subject of many experimental studies, including pressure drop, flow rate, mean velocity, velocity fluctuations and Reynolds stress profiles measurements (Bewersdorff and Strauss,1979; Bewersdorff,1984; Berman,1986).

Zakin et al (1979) studied the drag reducing behaviour of oil-in-water emulsions containing 50% or more of oil and reported that these emulsions showed significant reduction of friction in turbulent flow. Several polymer and surfactant drag reducers were tested in these emulsions, and high molecular weight polyacrylamides were found to be the most effective in further reducing the energy losses.

Quite recently, Madavan et al (1985) have shown that the microbubble drag reduction is a very important phenomenon, and by modeling it they have predicted that skin friction reductions as much as 50% can be obtained. Also, Povkh (1984) reported that the "bubble method" was a very promising and effective means for reducing friction.

2.3.2. Drag reduction by solid particle suspensions.

The friction reduction associated with suspended solid matter has received considerable attention for many years because of its large applications in transportation of coal, raw, sewage and sediment. According to Shenoy (1984), suspensions can be classified in two different types, depending on the nature of the particles:

1. Granular or nearly spherical particles.

2. Fibres.

The size distribution of particles in the suspension is an important parameter which influences drag reduction. Actually, the mechanism of drag reduction by solids suspended in flowing liquids has not been investigated, but it is found that in many cases drag reduction is greater with suspensions than with polymers. This indicates a possible additive mechanism for the Toms effect (Sifferman and Greenkorn,1981). The relative advantages of solid particle suspensions over polymers are the following:

a. They suffer no mechanical degradation, except some few cases (Vanusse et al,1979).

b. The solids can be added and removed from the flowing liquid with great ease.

More details on the subject are available in the works of Ellis (1970), Patterson et al (1969), Radin et al (1975) and McComb and Chan (1985).

2.3.3. <u>Drag</u> <u>reduction</u> <u>by</u> <u>surfactant</u> <u>solutions</u>.

Soap and surfactant systems have been the subject of a systematic study which has revealed many interesting aspects of drag reduction (Patterson et al,1969; Savins,1969; Shenoy,1984). There are basically three classes of surfactants, namely, anionic, cationic and nonionic, which show drag reducing properties.

a. <u>Anionic</u> <u>surfactants</u>.

(i) <u>Aqueous</u> <u>systems</u>: In his pioneering work, Savins (1967) made use of alkali metal and ammonium soaps at concentration 0.1% w/w and obtained a drag reduction of 30%. He observed that the addition of an electrolyte (KCl) resulted in an increase of drag reduction. Specifically, he performed pipe flow experiments and showed that the drag reduction percentage could be raised from 45% to 82% at a fixed wall shear stress of 150 dynes/ cm^2, by increasing the concentration of KCl from 3.5% to 10%. The amount of electrolyte was found to range from 2% to 14% in order to produce stable association colloids for drag reduction. He also observed an interesting stress controlled drag reduction effect, which was contrary to what was observed in the case of polymer solutions. The drag reduction occured at a critical shear stress which depended on the amount of electrolyte present. This stress controlled drag reduction phenomenon was found to be amazingly reversible. Savins also showed that the soap solutions he used were resistant to mechanical degradation. Palyvos (1974) reported that there is no chemical

degradation for this class of surfactants upon aging.

The effect of temperature on this type of drag reduction is considerable. Savins concluded that it is profitable to use a lower concentration of soap for greater efficiency if the ambient temperature is lower.

(ii) Nonaqueous systems: The first such systems studied in detail in a pipe flow apparatus were aluminium dioleate and aluminium palmitate soaps in toluene. It was found that they exhibited profound differences from the aqueous systems (Radin et al,1969; Shenoy,1984).

So, unlike the aqueous anionic surfactants, drag reduction did not occur until a concentration as high as 0.75% was reached. At this concentration, the viscosity was found to be two or three times that of the solvent. Also, the aged solutions were not as sensitive to mechanical degradation as fresh solutions. Contrary to Savin's results (1967), significant values of the first normal stress differences were observed in 1% solution of aluminium dioleate in toluene for values of shear rate between 2000 s^{-1} and 30000 s^{-1}. Furthermore, critical wall shear stress was not found for these solutions. In another study of similar systems, no time or shear degradation was found for concentrations above a critical value (Palyvos,1974).

McMillan et al (1971) noticed that the method of preparation of the disoap solutions strongly affected their turbulent flow characteristics. They also found that aluminium dioctoate was the best drag reducer among

soaps or polymers, in organic solvents.

The study of temperature effects on drag reduction by these additives showed that larger percentages of drag reduction correspond to lower temperatures.

It was also shown that large agglomerates or micelles caused appreciable drag reduction by affecting both viscosity and viscoelasticity of the nonaqueous solution.

Very interesting experimental studies on the drag reducing behaviour of soap colloids have been made by Hershey et al (1975). They studied toluene solutions of straight and branched chain aluminum disoaps in laminar and turbulent flow. They found that the branched chain disoaps were more effective drag reducers than the straight chain disoaps. Aluminum dioctoate required the lowest concentration for drag reduction (0.08%), and aluminum di-2-methylundecanoate showed extreme stability with time and shear.

Finally, the presence of light, moisture and tracers of other substances have a significant effect on the performance of such systems, as reported by Baker et al (1970) who performed experiments with disoap-hydrocarbon solutions.

b. Cationic surfactants.

The rheological behaviour of aqueous solutions of the cationic surfactant hexadecyltrimethylammonium bromide (HDTAB) in an equimolar mixture with 1-naphtol was first described by Nash (1956). These solutions formed viscoelastic gels. He found that the Swirl Decay Time (SDT) of the solution is a very rapid and useful method for the characterization of its viscoelasticity. Actually, in order to find the SDT of a solution it suffices to set up a swirling motion in a fixed volume of solution and measure the time taken for the mean motion to be reduced to zero for the first time, before recoil sets in. Also, Nash showed that the optimum mixture for viscoelasticity was not far from equimolar.

Zakin et al (1971) investigated the drag reducing ability of HDTAB-naphtol mixtures dissolved in water. They found experimentally that at about 0.18% total soap concentration maximum drag reduction occured over the whole range of flow rates. By working at a temperature range between 26°C and 48°C, they observed that the drag reducing behaviour of these mixtures was completely lost after the 48°C test. This loss was permanent, and the solutions showed no drag reduction characteristics even when cooled to 26°C. The recent studies of Elson and Garside (1983) showed that the drag reducing properties of aqueous cationic soap solutions are characterized by the critical wall shear stress, above which drag reduction ceases. They examined the temperature effects and

found that the optimum temperature for maximum wall shear stress for mixtures of alkyltrimethylammonium halides with 1-naphtol in water is at or near the Kraft point of the pure soap, i.e. the critical temperature below which micelles will not form (Rosen, 1978). According to these authors, the drag reducing properties of the soap - 1-naphtol solution may be explained by the interaction of the 1-naphtol with the cationic soap micelles, allowing very long rod-shaped micelles to form.

The cationic surfactants are mechanically stable, but their disadvantage is that they degrade thermally and chemically.

c. Nonionic surfactants.

Zakin and Chang (1972) observed significant amounts of drag reduction in the pipe flow of several aqueous nonionic surfactant solutions at a certain range of temperatures. Actually, the nonionic surfactants have an upper and a lower temperature limit for solubility in water. They noted that the solutions studied (nonionics formed from straight-chain alcohols and ethylene oxide) were effective drag reducers near their upper critical solubility temperature or cloud point. That is so, because as the temperature was raised and these systems approached their clouds points, large agglomerates were formed with molecular weights comparable to those of high polymer drag reducers. The resultant solutions had high relative viscosities and gave pronounced drag reducing behaviour. The increase of temperature changed the drag reducing behaviour from dilute to concentrated. Dilute behaviour refers

to one in which there exists a transition period even after fully developed turbulent flow is reached, before the solution shows drag reduction. When no such transition period is present, we have concentrated behaviour. By adding some electrolytes and particularly those containing polyvalent anions like sulfate, thiosulfate or phosphate, they could obtain concentrated drag reduction from what was initially no drag reduction. Also, these electrolytes were effective in lowering the cloud point.

Zakin and Lui (1983) studied the drag reducing behaviour of linear primary alcohol ethoxylate nonionic surfactants in aqueous solutions and found that mechanical stability is enhanced as concentration of surfactant increases approaching the cloud point, and as electrolyte concentration increases at temperatures below the cloud point. They reported that this type of drag reducing additive is repairable.That is, after it is degraded mechanically it recovers its drag reducing ability when it reaches a region of low shear forces. Mechanical degradation appeared to begin at the same critical wall shear stress independent of tube diameter.

In general, we can say that nonionic surfactants are both mechanically and chemically stable. Shenoy (1976) found that these types of additives in the presence of electrolytes have excellent potential for drag reduction at high temperatures.

d. Comparison of different types of surfactants.

Although the different types of surfactants discussed above have both advantages and disadvantages, there are some pronounced differences which lead one to choose the appropriate type for a specific application.

In addition to the above analysis, another basis for comparison is the behaviour of these solutions in the presence of calcium anions. Both cationic and nonionic surfactants do not precipitate in the presence of these ions, therefore they can be used in all impure water solvents, sea water or brakish water. On the other hand, anionic surfactants do precipitate under these conditions, but they are inexpensive, contrary to the other types.

2.3.4. Drag reduction by biological additives.

These types of additives haven't received enough attention because their potential for practical use presently appears to be limited. However, they have very interesting drag reducing properties.

In a search for new, more effective drag reducing polymers, Kenis (1971) tested polysaccharides (polymers of repeating sugar units) from sea weeds, microscopic algae, and the bacteria. He reported (1968) that many different bacteria produce friction-reducing polymers and he concluded that the great chemical and structural diversity makes the

bacterial polysaccharides an interesting class of polymers for drag reduction studies. These polymers (xanthomonas campestris, guar gum) were found to show long term stability and their superiority to "typical" drag reducing polymers like polyethylene oxide, was evident. His degradation studies showed that the xanthomonas campestris is a better and more durable additive than guar gum.

One of the most important biological additives is the DNA. It is actually a random coiling polyelectrolyte, which has extended conformation in solution. This material has been characterized by Sakamoto et al (1976). Parker and Hedley (1972) tested solutions of DNA and found that the drag reduction was not so great. They reported that the drag reduction was significantly reduced when these solutions were denaturated by heating or by changing the pH value. Drag reduction pipe flow experiments with DNA have been also carried out by Berman et al (1978). Finally, North and Champion (1974) have extensively studied the hydrodynamic degradation of DNA and found that it depends on both the shear rate and the time of shear.

Other popular drag reducing biological additives are chaetoceros didymus, protocentrum micans and fish slimes (Palyvos,1974).

2.4. The proposed theories of drag reduction.

The objective of the drag reduction studies is to seek a mechanism which can predict the large changes in the turbulent flow caused by the presence of minute quantities of additives.

Drag reduction is best described by observations of gross flow rate and pressure drop in turbulent pipe flow (Berman,1978). So, most of the existing theories for the prediction of the Toms phenomenon deal with this particular type of flow and with polymers as additives, since these are the most extensively studied drag reducers.

The first effort to explain the behaviour of macromolecules was made by Oldroyd (1948) who suggested that polymer molecules, during flow, affected the region near the wall most strongly , and proposed the "slip-at-the-wall" theory. Based on Oldroyd's theory, Toms (1948) explained his drag reduction experiments by proposing the idea of a shear-thinning wall layer with an extremely low viscosity which resulted in lower friction coefficients for the polymer solutions than for the solvents. The theory of Toms, however, was completely shattered (Barnes and Walters,1968).

Another mechanism was suggested by El'perin et al (1967) who developed the wall adsorption theory, based on some experimental observations. In this mechanism, polymer molecules are assumed to adsorb on the flow boundaries and subsequently affect the hydrodynamics of the

flow near them. However, it was shown that there is no possible relationship between polymer adsorption surfaces and drag reduction, and so, Hand and Williams (1973) came out with the theory of adsorbed-entangled layer. They demonstrated the existence of this layer by flow rate reduction experiments with dilute polymer solutions and proposed that it is responsible for much of the drag reducing behaviour. However, this left several features of the Toms phenomenon unexplained (Gyr and Mueller,1974; Ayyash and McComb,1976).

Patterson and Zakin (1968) developed a viscoelastic model for calculating reductions in turbulent bursts (a brief discussion on turbulent bursts and related problems is presented in chapter 2.6.). They evaluated the normal stress differences by measuring the thrust from a jet of the viscoelastic solutions. Their calculations were compatible with their experimental results, but could not be relied upon, as the solutions used for these experiments were much more dilute than those used for the thrust experiments.

Ruckenstein (1973) suggested that the drag reduction is due to the viscoelasticity of the polymer solutions. Actually, he proposed that the wall shear stress is smaller for viscoelastic fluids than for the corresponding Newtonian, and that the renewal of the elements of liquid along the wall takes place more slowly in the case of viscoelastic than in that of Newtonian fluid.

Fortuin and Klijn (1982) discussed in detail the relationship between drag reduction and the random surface renewal in turbulent pipe flows.

Another possible explanation for drag reduction could involve the idea of elongational flow. It is likely that the addition of minute quantities of polymer to a solvent leads to a substantial increase in the resistance to elongational flow, thereby resulting in less turbulent bursts and thus lowering the turbulent drag (Hunston and Ting, 1975). Lumley (1967) postulated that it was the molecular entanglements which extended cross-stream and resisted the formation of streamwise vortices, and that caused an increase in the sublayer thickness of the boundary layer, and thus, resulted in drag reduction.

The stretching of macromolecules is induced by the mutual interactions of convoluted vortex filaments starting as nonlinear laminar oscillations close to the wall. The drag reducers help to delay the breakdown of these oscillations into turbulence. The net effect is a partial absorption of the kinetic energy of the vortices, thereby allowing them to grow in size and penetrate further away from the wall before being unstable, thus resulting in an increased sublayer thickness and a drag reduction. Gordon (1970) showed that polymer molecules suppressed the turbulent bursts and thereby increased the resistance to stretching. That resulted in an inhibition of the magnitude of bursts and, hence, the flow became less turbulent.

The theories related to elongational flows and stretching are parts of the more general polymer-structure-and-conformation approach to the study of drag reduction. One of the pioneering works in this field is that of De Gennes (1974), who has shown that under high shear, the flexible polymer molecules can abruptly unwing from the random coil configuration to the extended or stretched configuration. This coil-stretch transition can be explained in terms of the hydrodynamic interactions, which are reduced by stretching. This concept is very useful in explaining how drag reducing molecules interfere physically with the smallest hydrodynamic eddies.

The investigations of Hinch (1977) are also very important. He suggested that in "strong" flows (Tanner,1985), such as turbulence, randomly coiled macromolecules might become nearly fully extended. His theory predicted that a dilute polymer solution has a high extensional viscosity but a low shear viscosity, a stress hysteresis and a slow stress relaxation. Finally, he speculated that the high extensional viscosity in strong flows is the main reason for drag reduction. In another work, Hinch (1976a,1976b) represents the polymer molecule as a flexible thread, and studies its distortion in a shear flow. His computations have very significant implications in drag reduction.

Some very important contributions in the areas of coil-stretch transition of polymers in dilute solution and elongational flows have been made by Denn and Marrucci (1971), Everage and Gordon (1971), Tanner

(1976), Onuki (1985) and Dash et al (1985).

One very comprehensive structural hypothesis for the mechanism of drag reduction was postulated by Lumley (1969,1973,1977). According to him, the elongation of the macromolecule initiates a sequence of changes in mean and turbulent flow structures and causes a reduction in drag. His approach is statistical and doesn't require a detailed mathematical theory for turbulent boundary layers. The basic turbulent structure is assumed to be similar to that in Newtonian boundary layers in that there exist three regions: The viscous sublayer, which is the closest to the wall, and where the dissipative forces dominate, the buffer layer, which is next to the viscous, and the logarithmic region. Large eddies are formed in the viscous sublayer and extend into the buffer layer (Bakewell and Lumley,1967). He postulates that at sufficiently high wall shear stress polymer molecules are expanded in the flow outside the viscous sublayer due to the fluctuating strain rate and cause an increase in the effective viscosity, which , in turn, damps small dissipative eddies. Since the Reynolds stress in the buffer layer is basically produced by the small eddies, momentum transfer is reduced in this region due to the reduction in the small scale disturbances. This results in a delay in the reduction of the mean profile slope to a point farther from the wall, and thereby in a thickening of the wall region. This mechanism is consistent with almost all of the existing experimental results (Lumley and Kubo,1984), but leaves unexplained such features as the bursting period for large eddies.

Among the many other mechanisms which have been proposed to explain the Toms phenomenon, the development of a resistance to vortex stretching due to the presence of the additives, is of particular interest. Gadd (1968) suggested that the larger polymer molecules with larger relaxation times would probably affect large eddies with less intense stretching rates, and cause their more rapid decay. However, Gyr (1968) pointed out that the vortex stretching inhibition was effective only in the case of the smallest eddies near the wall. The vortex stretching inhibition has been the subject of many studies (Kuo and Tanner,1972).

The structural hypothesis of Landahl (1977) was in agreement with Lumley's theory, although his approach was completely different. He applied classical hydrodynamic stability theory to the turbulent boundary layer and developed a so-called "two-scale model". He applied his model to drag reduction by considering the turbulence to consist of a coupled motion at two disparate scales: A primary one of large scale, of the order of boundary layer thickness, and a much smaller secondary one, of the order of the viscous sublayer thickness. He proposed that the elongation of added polymer molecules stabilizes the small scale field, and this inhibited turbulence production. His mechanism is much more specific than Lumley's and is consistent with existing experimental results, although some of its aspects cannot be supported by them.

Another very important approach to explain the mechanism of drag

reduction was that of Virk (1971,1975). He introduced the notion of the elastic sublayer, which, according to him, is characteristic of the Toms phenomenon. Actually, he has suggested that the stimulation of the polymer molecules by a turbulent shear flow creates a zone called the elastic sublayer, which originates at the onset of drag reduction, which could grow in size with increasing drag reduction and eventually occupy the entire pipe cross-section at maximum drag reduction. According to him, all drag reduction observations can be related to the properties and extent of the elastic sublayer.

The mean flow model of Virk, along with his terminology, is shown schematically in figure 5.

In the elastic sublayer the velocity profile can be approximated by:

$$U^+ = 11.7 \log(y^+) - 17.0 \quad \text{for } y_v^+ < y^+ < y_e^+$$

where the superscript + refers to normalized quantities, and the subscripts u and e refer to the outer edge of the viscous and the elastic sublayer, respectively.

Virk also proposed (1970,1975) the idea of the maximum drag reduction asymptote, beyond which no further viscous drag reduction is found (figure 6). This universal maximum drag reduction asymptote is insensitive to polymeric parameters and is given by the expression:

$$1/\sqrt{f} = 19.0 \log(Re\sqrt{f}) - 32.4 \ .$$

The drag reduction phenomenon appears bounded between the Prandtl-Karman (or Blasius) law for Newtonian turbulent flow (which is given by the

expression: $1/\sqrt{f}=4.0$ $\log(\text{Re}\sqrt{f})-0.4$) and the maximum drag reduction asymptote. For the drag reduction regime, in which the friction factor relation depends upon the nature of the polymer solution, Virk suggested the approximate expression:

$$1/\sqrt{f}=(4.0+\delta) \log(\text{Re}\sqrt{f})-0.4-\delta \log(1.41) dW'$$

where $W'=u_\tau'/v_s$, the superscript $'$ referring to the onset of drag reduction, and δ being polymer solution parameter. The term u_τ is the friction velocity, defined as $u_\tau=\sqrt{(\tau_w'/\rho)}$ (Virk,1975a).

Berman (1978) pointed out that there is no well-defined maximum drag reduction asymptote . So, there are some experimental results consistent (Virk,1975a) and some other inconsistent with this asymptote (Kubo and Lumley,1980).

In addition to the theories for the investigation of the mechanism of the Toms effect, many other theoretical studies have been made. The objectives of these studies were: Calculation of turbulent flows of dilute polymer solutions (Durst and Rastogi,1977; Tiederman and Reischman,1976; Shenoy and Talathi,1985), interpretation of drag reduction in wavy laminar films of polymer solutions (Dutta and Mashelkar,1983), application of thermodynamics to drag reduction (Jones and Penglais,1980), reduction of the secondary motion in curved tubes by polymer additives (Tsang and James,1980) and turbulent flow calculations of mildy elastic drag reducing fluids through a straight tube rotating around an axis perpondicular to its own (Shenoy,1986).

2.5. Morphology of drag reducing systems.

In the case of polymer systems it is generally agreed that the morphology of a polymer in solution resembles a loose three-dimensional network consisting of variously extended macromolecule segments (Savins,1967). A review of the configurational properties of polymers in solution has been published by Flory (1975).

Several studies have been made in order to determine the molecular parameters of the drag reducing polymers, and have been mentioned in the earlier sections of this work, where some of these parameters have been discussed. In addition to them, there are the recent studies of Berman (1975,1980), Sandjani et al (1980), Virk and Baher (1970) and Jones (1976a). It has been found that, for drag reduction to occur, the polymer molecules should be flexible, loosely coiled and long-chained (Hand and Williams,1971; Little,1971) with small side groups. Lee et al (1974) conducted experiments in which they found that if they took rigid fibres and random coil polymers, each of which was a moderately good drag reducer on its own, and combined them, they could get friction reduction up to 95%.

The well known phenomenon of onset of drag reduction in pipe flows of dilute polymer solutions has been the subject of many studies because of its importance (Virk and Merrill,1969; Virk,1975a). Virk et al (1966) postulated that onset occurs when the ratio of the turbulent length scale, v/u_τ, and a characteristic polymer length scale (the root-

mean-square radius of gyration, R_G) reaches a critical value (length scale hypothesis). Fabula et al (1966) and Lumley (1969) proposed that onset occurs when the ratio of the smallest flow time scale, ν/u^2, to the polymer molecular relaxation time, λ_1, is of order one (time scale hypothesis). This characteristic relaxation time (Ferry,1980) is of particular interest -from the molecular point of view- for the drag reduction studies, since it is related to the extension of the polymer molecules (Lumley,1971). Berman and George found that the time scale onset hypothesis is more consistent with experimental data than the length scale onset hypothesis, and therefore, it should be regarded as correct. Berman (1977b) verified these findings and showed that after onset, in turbulent pipe flow of solutions of extended macromolecules, drag reduction is related to the lifetime of the large eddies, D/u, where D is the pipe diameter, and reported that the magnitude of drag reduction, after the molecules were extended, increased with pipe diameter. It has been also shown, that after onset drag reduction is dominated by small amounts of the highest molecular weights, for polydisperse polymers (Berman,1977a). Sharma et al (1979) have studied the effect of pipe diameter and its concentration on the onset of drag reduction. Hunston (1976) has related molecular weight distributions to the onset of drag reduction, maximum drag reduction and shear stability.

Related to the onset of drag reduction is the concept of early turbulence, which, according to Forame et al (1972) is the departure of the flow of dilute polymer solutions from the Newtonian behaviour under

conditions of steady laminar shear. Little et al (1975) suggested that this concept is important in understanding the Toms phenomenon.

If one compares the experimental results for drag reduction with polymers and with surfactants, one can easily conclude that the behaviour of the additives in the two cases is different. Actually, the soap solution exhibits drag reduction at low wall shear stress and beyond a certain critical value the solution shows normal turbulent behaviour. More specifically, Bewersdorff and Ohlendorf (1985) performed experiments in order to investigate the effect of drag reducing surfactants on the structure of turbulent pipe flows. They have found that there are three characteristic regimes in the turbulent pipe flows of surfactants: For low Reynolds numbers, in the turbulent flow regime (region 1) the micelles act in a similar way to polymer molecules. At higher Reynolds numbers, in the flow regime in which the friction factor seems to be independent of the Reynolds number, the turbulence might be influenced in the same way (region 2). The most dramatic changes in the turbulent structure are found in the medium flow regime (region 3), in which the friction factor approaches the Virk's maximum drag reduction asymptote. It has been also shown that the limits of these three flow regimes can be influenced by changing the temperature and/or concentration (Ohlendorf et al,1984).

On the other hand, polymer solutions exhibit small drag reduction at low Reynolds numbers, and large drag reduction at large Reynolds

numbers. This contrasting drag is due to the significant morphological difference between micellar and polymeric systems.

All surfactant molecules or ions, at concentrations above a minimum value characteristic of each solvent-solute system, associate to form particles called micelles. Among the many types of micelle structures suggested, the most common are the spherical and the lamellar. The spherical micelles are said to exist only in dilute solutions and the lamellar are favored in concentrated solutions. In fact, several different structures exist. It is possible for transition from one type to another to occur. Which of these structures exists in any particular system depends entirely on the system parameters such as chemical nature of the surfactant, the solvent, the presence of salts or other materials and temperature and concentration of each component (Savins,1969; Shenoy,1984).

Since drag reducing solutions show viscoelasticity with increased concentration of the additives, the viscoelastic behaviour of the surfactants is very important in the drag reduction studies (Ulmlus et al,1979).

An attempt to investigate the effect of the morphological structure of a complex soap in its drag reducing behaviour has been made recently by Myska and Simeckova (1983) who discussed the shape of the micelles of this soap and confirmed the existence of fibrillous structure.

2.6. The experimental evidence.

Extensive measurements with all sorts of instrumentation have been made of mean and fluctuating quantities in drag reducing flows in order to investigate the nature of the Toms effect.

The effects of molecular parameters (like molecular weight distribution of polymer, degradation, concentration, type of additive) and other important parameters (like pipe diameter and temperature) have been considered in an attempt to elucidate the nature of the additives (Little et al,1975; Berman,1980; Interthal and Wilski,1985).

Measurements of the mean velocity profile were the first to be made, and are the most numerous in the literature. Regarding the methods employed for these measurements, the data obtained with hot-wire anemometers and Pitot tubes are subject to considerable errors and, therefore, are not reliable (Kubo and Lumley,1980; Virk et al,1967). The Laser Doppler Anemometry measurements are the most accurate and the most commonly used in the recent years (Buchhave et al,1979; Allan et al,1984; Schummer and Thielen,1980). In figure 7, the mean velocity profiles are represented in coordinates normalized with wall variables. It can be concluded that any profile has the same asymptotic behaviour at the wall. Also, the viscous sublayer is unchanged from the Newtonian case, while the buffer layer contains all the observed differences between the drag reducing and the Newtonian flows. Furthermore, the velocity profile deviates from the $U^+=y^+$ line at around $y^+=8$ - 10.

Finally, in the buffer layer the profile doesn't follow the Virk's maximum drag reduction asymptote. This means that, as mentioned above, there is no well-defined maximum asymptote for drag reduction.

It is worthy to point out that the motion of fluid in turbulent flow was previously thought to be completely chaotic. Such a motion is best described by stochastic models. However, research in the last decade has shown that organized events of describable nature are present in the seemingly chaotic fluid movements. Some of these events are the so-called "bursts". It is shown that both the rate and the size of turbulent bursts are influenced by the presence of dilute polymer solutions (Tanner,1985). A nice discussion and experimental work on turbulent bursts in drag reducing flow is presented by Achia and Thompson (1977). They showed that, for the case of dilute aqueous solutions of Separan AP-30, the rate of turbulent burst decreased with drag reduction, and the lateral burst spacing increased with drag reduction.

Today, the turbulent bursts are one of the most active research areas in turbulent flows and drag reduction. Actually, a very interesting question concerns the bursting period in the turbulent boundary layer. What is in question here specifically, is the mechanism by which the burst of Reynolds stresses produces a new vortex pair (Lumley and Kubo,1984; Donohue et al,1972). By answering this question we can increase our understanding of the nature of the turbulent

boundary layer and drag reduction. So, any measurement that clarifies the behaviour of the bursting period in drag reducing flows is of primary interest.

The measurements of turbulence intensities using Laser Doppler Anemometry (Mizushiva and Usui,1977) can be divided in three headings:

a. Streamwise intensity profile: All experimental results show that the peak in turbulence intensity is shifted to higher y_+ values as the drag reduction increases, and its value doesn't change much when the Reynolds number is high. The intensity is reduced in the region $y_+ < 20$. We can conclude that, in polymer flows, the bursting phenomena, which are mainly responsible for the turbulence production, take place further away from the wall region, compared to the solvent flow (figure 8).

b. Transverse intensity: The few measurements available indicate that in the core region the intensity is the same as that of the solvent, while in the buffer layer it is lower.

c. Frequency spectra of the fluctuating signal (wall shear stress and velocity fluctuations): The measurements indicate that the spectral density functions for solutions of drag reducing polymers show slight attenuation of the high frequency components. Other experimental results show that the non-dimensional streak spacing increases as the drag reduction increases. Flow visualization experiments indicate that the bursting period doesn't change from that of Newtonian fluids at the same shear velocity. However, the autocorrelation method (Berman,1978) suggests an increase in the bursting period in polymer flows at the same

shear velocity.

Another interesting experimental observation is that drag reducing polymer flows undergo transition at a lower Reynolds number than Newtonian flows (Kubo and Lumley,1980).

Of particular interest are the electrochemical methods of turbulence measurement (Hanratty and Chorn,1977). These techniques have been developed to study flow fields and scalar transport. The principle involved in them is that an electrochemical reaction is carried out on a solid electrode surface held at a high enough voltage, so that the process is mass-transfer controlled. Then, measurement of the electric current is directly proportional to the rate of mass transfer to the test electrode.

In addition to the pipe flow measurements mentioned above, many other types of flows have been considered. Among them, channel flows have been the subject of many studies (Reischman and Tiederman,1975; Tiederman et al,1985; Kwack et al,1981). Hoyt and Taylor (1977) studied the effect of polymer additives in the structure of turbulence in a water jet. Walters et al (1971) considered the case of drag reduction in helically coiled pipes. Similar studies have been made by Mashelkar and Devarajan (1976,1977), and very recently by Tomita and Yokoyama (1985), who verified experimentally the theoretical predictions for frictional losses in curved pipes. Rubin and Elata (1971) studied the turbulent flow of dilute polymer solutions through an annulus. Jones et al

(1976a,1976b) and Jones (1976b) reported results for the flow of dilute aqueous polymer solutions through porous media and between rotating coaxial cylinders (Couette flow). McComb (1974) and McComb and Ayyash (1979) investigated the effect of drag reducers on free oscillatory flow in U-tube manometers. Quraishi et al (1977) have studied the influence of the addition of drag reducing polymers and fibers on mixing and dispersing in mechanically agitated vessels. Specifically, they have determined the mixing times and the critical rpm at which complete suspension of solid particles occurs, under the presence of these additives. The measurements of the drag force on small circular cylinders in dilute polymer solutions performed by James and Gupta (1971) and the studies of the flow characteristics of some dilute macromolecular solutions in flows around spheres made by White (1969) are examples of the experimental studies curried out for external flows.

Among the many other studies made in order to explain the behaviour of long-chain polymers in turbulent flows of particular interest are those related to stability of pipe flows and grid-generated turbulence (Kubo and Lumley,1980).

2.7. Rheological characterization of the additives.

Although it is generally agreed that turbulent drag reduction by polymers is a consequence of the viscoelastic properties of the dilute polymer solutions, specific data on these properties, and especially on the elastic, or any relevant quantitative relations are rarely available. The reason is that the very low concentrations of these solutions make the characterization of their rheological properties very difficult. The difficulty arises from the fact that the viscous and elastic forces developed by these solutions are relatively small and, therefore, the measurement of the various rheological material functions is considerably more difficult than for concentrated solutions or for molten polymers. Nonetheless, it has been shown that these solutions are nonlinear viscoelastic fluids (Argumedo et al,1978).

In the past years considerable effort has been made to measure both the steady and the dynamic properties of dilute drag reducing solutions. Darby (1970) noticed the importance of measuring the elastic properties from unsteady response to predict or analyze fluid behaviour in turbulent drag reducing flows. He was able to determine the apparent viscosity and first normal stress difference of dilute polyacrylamide solutions as a function of the shear rate by using conventional viscometers. He used a cone-and-plate Weissenberg rheogoniometer (Middleman,1968).

However, an attempt to characterize the elastic properties of these solutions by conventional oscillatory response methods was not successful, so he employed a specially designed transient rheometer. He and his coworkers have shown how to use data for the apparent viscosity, the normal sresses and the characteristic time constants, in order to predict the friction loss in drag reducing turbulent pipe flows (Tsai and Darby,1978; Darby and Chang,1984b).

Chang and Darby (1983) studied the effect of shear degradation on the rheological properties of polymer solutions. They found that shearing has a greater effect on the low shear viscosity of these solutions than it has on their elastic properties, resulting in a greater degree of drag reduction for the sheared than for the fresh solutions. At lower concentrations, however, the degree of drag reduction has been observed to decrease with degradation (Darby and Chang,1984a). This latter observation was in agreement with Ting's observations (1982). But, besides the concentration, there are many other factors influencing the relation between drag reduction and degradation, like the type of polymer and the pipe diameter.

It is clear from the material presented above, that the nonlinear viscoelastic properties of the very dilute drag reducing polymer solutions cannot be characterized by conventional methods. There is certainly a need to seek for new methods of characterization for these solutions. Such a method will be presented in the next chapters.

2.8. Heat and mass transfer studies.

The problem of turbulent heat and mass transfer in the presence of drag reducing additives has attracted considerable attention in recent years. From the work done in this area it can be concluded that additives have an equally pronounced effect on such transport processes as they do on momentum transport.

Ghajar and Tiederman (1977) made some important contributions to the heat transfer studies by showing how to predict heat transfer in drag reducing flows of polymer solutions.

It has been found that the Nusselt number of drag reducing flows decreases whenever the friction factor does. Experimental evidence with many different polymer solutions showed that onset of heat transfer reduction occurs later than the drag reduction onset. In pipe flows, the increase of thermal resistance in the buffer zone has been regarded as the main cause of the turbulent pipe flow heat transfer reduction in polyox and polyacrylamide solutions.

A number of investigators (Gupta et al,1967; Marrucci and Astarita,1967; Smith et al,1969) have established that drag reducing polymers can cause a reduction in the rate of turbulent heat transfer between a wall and aqueous solutions with Prandtl numbers in the range of 5 to 10.

Heat transfer measurements in rough pipes showed that the overall heat transfer coefficient for polyox solutions decreases with Reynolds number rather quickly. That was in contrast to the case of pure water solvent and guar gum solutions (Mizushina et al,1975; Taylor and Sabersky,1974).

A very interesting topic in heat transfer is that of suspension flows, and Moyls and Sabersky (1975) have studied heat transfer in asbestos-water suspensions. Their results have shown spectacular reductions in heat transfer from this highly drag reducing suspension.

Of great interest are the nucleate pool boiling heat transfer studies with polymeric additives since they elucidate another area related to the drag reduction phenomenon. The nucleate boiling curves obtained for aqueous polymer solutions were shifted to higher temperature differences when compared with the boiling curve of pure water. (Paul and Abdel-Khalik,1983). Rouai and Abdel-Khalik (1983) investigated the relation between critical heat flux and minimum film boiling temperature for different drag reducing polymer solutions.

An excellent review of heat transfer reduction due to polymers and fiber suspensions has been given by Dimant and Poreh (1976).

The motivation for studying the absorption and diffusive transport of various solutes in solutions of drag reducing additives is due to its significance, both in industrial and biomedical applications, where

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biological media are involved. An extensive review of the mass transfer studies up to 1974 is given by Palyvos (1974).

McConaghy and Hanratty (1977) have studied experimentally completely developed and entry region mass transfer rates in turbulent pipe flow of drag reducing polymer solutions using electrochemical techniques. The percent change in the fully developed mass transfer rate at a given volumetric flow was found to be greater than the percent change in pressure gradient. The decrease in the mass transfer rate caused by the addition of drag reducing polymers was associated with changes in both the turbulence close to the wall and the Schmidt number. Similar experiments have been carried out by Sidahmed and Griskey (1972), and Shulman et al (1977).

Very recently, Vassiliadou et al (1986) studied experimentally the effect of dilute solutions of polyacrylamide on mass transfer fluctuations by using electrochemical techniques. They have shown that these drag reducing polymer solutions decrease the magnitude and the frequency of the fluctuations in the mass transfer coefficient.

Virk and Suraiya (1977) have studied both theoretically and experimentally mass transfer in dilute polymer solutions under conditions of maximum drag reduction. They have proposed the so-called "elastic sublayer analogy". Specifically, their mass transfer results along with the elastic sublayer model for drag reduction, developed earlier (Virk,1971), lead to the formulation of an "elastic sublayer"

analogy for scalar transport during drag reduction. The predictions of this analogy, at the two extremes of low and maximum drag reduction, agreed approximately with the experimental results available.

Finally, Smith et al (1982) have measured the mass transfer in both fresh and degraded dilute aqueous solutions of polyox in turbulent pipe flow. They found that shear degradation increases the diffusion coefficients. Also, the mass transfer rates for polymer solutions were found to be much lower than those for the solvent. Finally, those solutions which showed the lowest friction factors also showed the lowest mass transfer rates.

3. PROPOSED RESEARCH

The question which arises from the previous sections is what studies, complementary to the theoretical and experimental work already done, will increase our understanding of the mechanism of turbulent drag reduction. One of the most interesting problems is the effect of polymer molecular parameters on drag reduction (Ting,1982; Zakin and Hunston,1980; Ozari,1981a; Hlavacek et al,1976), and related to this problem is the question of determination of the rheological properties of very dilute polymer solutions, and their use as a means of characterization of drag reducing polymers. It is known that sufficiently dilute solutions (less than 100 ppm per weight) often appear to be essentially Newtonian in their viscous behaviour, and furthermore tend to exhibit a dependence of drag reduction on concentration and degradation which is just the opposite to that exhibited by the more concentrated solutions (which exhibit non-Newtonian behaviour). Hence, the rheological characterization of such dilute solutions is a challenging problem (Darby,1984; Dschagarowa and Bochossjan,1979). Also, by using very dilute solutions one can reach the

concentration necessary for maximum drag reduction.

By measuring the rheological properties of a dilute polymer solution, one can associate them with the deformation of the polymer molecules in flow, and thereby, infer results about the drag reduction mechanism. The choice of the constitutive equations which are appropriate for the drag reducing flow of dilute polymer solutions is critical (Darby,1970). By using such equations coupled with equations of motion for a specific flow situation and by knowing the viscometric functions of the polymer solutions used, one may end up with predictions of their elastic parameters.

Among the many types of drag reducing polymers, there are some which are preferred with respect to others and are recommended as better drag reducing systems. Such polymers are the polyacrylamides (Elliot and Stow,1971), polyethylene oxide (Virk et al,1967; Virk,1975), xanthan (Rochefort et al,1984), guar (Deshmukh et al,1985), polyisobutylene (Hershey and Zakin,1967) and polystyrene (Fuller and Leal,1980).

Shenoy (1984), Patterson et al (1969) and Savins (1967) have reported that surfactants are very important drag reducing additives, because they don't degrade in flow. Until recently, surfactants have not received much attention as drag reducing agents, but recent work indicates that they have considerable potential.

The proposed research program is focused on the topics mentioned

above and intends to make some contributions to the drag reduction mechanism problem by investigating the molecular behaviour of the different additives. This program will be presented in the next sections, where each topic is described in more details.

3.1. On-going work.

The first goal of this proposal is to characterize the very dilute drag reducing polymer solutions by studying their rheological properties.

At this point we should recall that the drag reducing flows are non-viscometric. As a consequence, three viscometric functions (shear viscosity, first and second normal stress differences) are not enough to completely describe the flow behaviour (Schowalter,1978). In addition, one or more characteristic times are needed. The idea of using these time constants comes from the fact that among the very important properties of non-Newtonian fluids is the "springiness" which they exhibit in time dependent flows. Thus, by observing the fluid behaviour in unsteady flows, one should be able to determine appropriate time constants.

Since the drag reducing polymers, as well as most fluid-like materials, exhibit nonlinear viscoelastic response, an appropriate nonlinear constitutive equation is required for the determination of the

elastic properties, and therefore, for the complete characterization of the dilute polymer solutions.

Chang and Schowalter (1974) investigated one classical flow that illustrates the features needed for the study of rheological properties of such solutions. It is the acoustic streaming generated in a fluid by an oscillating cylinder.We use in our study this type of unsteady non-viscometric flow.

3.1.1. Background.

The steady secondary flow which is induced when a long circular cylinder (or any other solid boundary) oscillates in a direction transverse to the cylinder axis, or when a fluid oscillates near a fixed cylinder, is a very interesting type of flow, because, due to the interaction of the nonlinear inertial terms in the equation of motion, time independent outputs result from time dependent inputs. This steady secondary flow in incompressible Newtonian fluids is also called acoustic streaming (Rayleigh,1945; Schlichting,1968; Batchelor,1973). This steady streaming has been studied extensively by Andrade (1931) and Holtsmark et al (1954), who carried out experiments with air oscillating near a fixed cylinder in a Kundt's tube. Some other researchers reported results for the case of an oscillating cylinder in fluid at rest (Skavlem and Tjotta,1955; Olsen,1956).

Stuart (1966), Riley (1967) and Wang (1968) summarized the theoretical results of the above studies. Kubo and Kitano (1980) analyzed theoretically the two-dimensional oscillatory flow of a cylinder in an unbounded viscous fluid at rest. Careful experiments for the case of an oscillating cylinder have been presented by Olsen (1956), Davidson and Riley (1972), Bertelsen et al (1973) and Bertelsen (1974).Westervelt (1953) showed theoretically that the steady streaming is the same for a cylinder oscillating in a quiescent fluid and for a cylinder fixed in an oscillating fluid. His statement was verified experimentally by Raney et al (1954).

Experiments in which the fluid oscillates have two major disadvantages: It is difficult to perform a truly sinusoidal oscillation of the fluid, and a high frequency of oscillation cannot be achieved easily. Therefore, the oscillating cylinder is preferred. Further details on the subject are available in the literature of nonlinear acoustics (Rooney,1981; Zarembo,1971; Nyborg,1965).

The study of steady secondary flows of non-Newtonian fluids is of particular interest, because, when one considers fluids with marked transient elasticity of shape, the nature of these steady flows can, under certain conditions, be completely different from what is encountered in a Newtonian fluid. This was first reported by Frater (1964), who studied the flow of a second-order fluid between torsionally oscillating disks. In 1967 the same person discussed the two-dimensional

secondary flow of an elastico-viscous fluid generated by a cylinder oscillating in a direction perpendicular to its length. Later, Chang and Schowalter (1974) presented the first experimental work in steady streaming due to an oscillating cylinder. They found that the direction of steady streaming can be opposite to that found for the the bulk of fluid when the experiment is performed with a Newtonian fluid. Their results are shown in figures 9 and 10. These results are in excellent agreement with the theoretical predictions of James (1977), Chang and Schowalter (1979) and Chang (1977).

Recently, Powell (1982) studied the acoustic streaming produced by the propagation of a finite amplitude planar acoustic wave in a non-Newtonian fluid. He predicted the change in direction of the streaming, with respect to the Newtonian case, and he attributed this change to nonlinear viscoelastic effects.

Similar studies in acoustic streaming of non-Newtonian liquids have been made by Rosenblat (1978). He was interested in the steady radial-axial flow generated in a non-Newtonian fluid confined between two infinite parallel planes by torsional oscillations of one of the planes. He predicted, that under certain circumstances the direction of the radial-axial (steady secondary) flow is opposite to that in a Newtonian fluid.

Chang and Schowalter (1976,1979) suggested that the steady secondary flow may be useful in characterizing very dilute polymer solutions,

since conventional viscometers are not appropriate for this particular case.

3.1.2. Motivation and Objectives.

As mentioned above, our principal research objective is to investigate the drag reducing behaviour of polymer solutions, taking advantage of the acoustic streaming phenomenon. Actually, the initial motivation for employing this specific type of flow for the drag reduction studies came from the earlier work of Chang and Schowalter (1974), discussed above. However, the relation between steady secondary flow and drag reduction is not obvious.

In fact, the high complexity of turbulent flow, and the random nature of the process - which is still poorly defined (Hinze,1975) -, are the major factors which inhibit a complete solution of the turbulent drag reduction problem. This is , actually, the principal conclusion from the literature review, presented in the earlier sections of this work.

However, one can gain a good understanding of this unusual phenomenon by approximating, in a sense, the turbulent flow with another type of flow, which is "well-characterized" (Scrivener et al,1979; Leal,1985).

We have decided to "approach" the turbulent flow conditions by the oscillatory flow, induced by a cylinder. This particular type of flow is time-dependent and, for the case of high frequencies of oscillation, a rapid shearing of the macromolecules in solution occurs.

In the oscillating cylinder system, both the primary and secondary flows can be described analytically. Our attempt is to investigate the behaviour of macromolecules in this flow. The way to do that is to use the extraordinary pattern of the resulting secondary flow, i.e. the reversal of the flow patterns when the process fluid changes from Newtonian to non-Newtonian. It is known that this effect is attributed to the elasticity of the non-Newtonian solutions. So, something happens in this oscillatory flow to the macromolecule, and results in the steady secondary flow. Actually, we can say that the secondary flow pattern corresponds to the response of the macromolecule to a rapid and unsteady shearing in the primary flow.

Thus, through a study of the flow induced by an oscillating cylinder we expect to study the coil-stretch transitional behaviour of flexible polymer molecules in dilute solution and, therefore, to understand what happens to the polymer molecules under conditions of turbulent flow.

Since the steady secondary flow is very sensitive even to very small amounts of elasticity (i.e. to dilute solutions), we can detect the deformation of a molecule in the primary flow, at very low concentrations. We believe, therefore, that we can relate these studies

to drag reduction. Actually, we expect to rank the dilute drag reducing polymer solutions with respect to their elastic properties, and investigate the mechanism of deformation of the macromolecules in the shear field imposed by the primary oscillatory flow in dilute solutions.

In conclusion, our objective is to study the behaviour of the macromolecules in the oscillatory flow described above, and use the characteristics of the resulting steady secondary flow to account for the drag reducing properties of dilute polymer solutions. Specifically, our ultimate purpose is to provide new tools to characterize drag reducing solutions by ascertaining relative degrees of elasticity.

In the next sections we proceed in the development of both experimental (basically, measurement of relaxation times) and theoretical (mathematical description of the problem for dilute solutions) parts, having always in mind our objectives determined in this section.

3.1.3. Experiments.

3.1.3.1. Flow System.

The first problem one deals with, is how to perform the oscillations. In the literature there are three methods available. In the first, the cylinder is put into a strong magnetic field and forced to oscillate perpendicular to its axis by means of an alternating

current (Olsen,1956; Bertelsen et al,1973; Tough et al,1964). In the second, a loudspeaker is used to oscillate the test cylinder (Tatsuno,1973,1981; Raney et al,1954). Finally, in the third method, the cylinder is forced to oscillate in the fluid by means of a scotch-yoke mechanism, which converts rotary motion into sinusoidal translation (Hamann and Dalton,1971; Minamizawa and Endoh,1984; Nagata et al,1985).

The disadvantages of the second method are a high sensitivity to external noise and the fact that it is hard to assure that, during translation, the cylinder remains in vertical position. The problem associated with the third method is that it fails at high frequencies, and is not appropriate for our application. Because of these problems, the first method seems to be more advantageous, and we have decided to use it in our application.

Our flow system is an adaptation of the device used by Chang (1975) and is shown schematically in figure 11. The inner cylinder is suspended on two thin bronze leaf springs and is placed in the center of the outer fixed cylinder (container). The springs are attached to the container wall as is indicated in the figure. Actually, each spring is welded to a movable screw which can slide along a copper rod. The copper rods are fastened to the container wall with two copper shafts on each side of the wall to prevent leakage. This method of attachement provides us the flexibility to adjust the inner cylinder as close to the center of the container as possible.

The inner cylinder is made of brass, and the outer cylinder wall is made of plexiglass (see figure 11). The top and bottom enclosures consist of glass. The bottom one is glued to the plexiglass container, and the top one can be removed in order to put the test liquid into the container. Glass was chosen for the ends because of its superior optical properties relative to plexiglass.

In order to obtain different results and to compare them with theoretical predictions, we use three different sizes of inner and outer cylinders. Three cylindrical brass rods of different diameters can be used for the inner cylinder, and three different sizes of plexiglass cylinders inserted into the container as shown in figure 12, for the outer cylinder. Each cylinder has a U-shape cut so that the lower bronze support can vibrate freely. The plexiglass collars are used to keep the inserted cylinder stationary and in the center position. The cuts of these collars are made so that they can slide into the bottom of the container, past the bronze supports, and the low support can vibrate freely. The outer collar diameter is equal to the inner diameter of the cylindrical container.

The dimensions of the different components of the flow cell are:
Inner cylinder: There are three cylindrical rods to be used, of height 11.43 cm each and diameters 0.3175 cm, 0.3962 cm and 0.4750 cm, respectively.
Outer cylinder (container): The inner diameter is 10.2565 cm and the

outer is 12.0142 cm. The height is 16.51 cm.

<u>Inserted cylinders and collars:</u> Three different sizes are used. The height of each cylinder is 11.43 cm and of each collar 2.54 cm.

<u>First size.</u>

Cylinder inner diameter= 3.7617 cm

Cylinder outer diameter= 4.4272 cm.

Collar inner diameter= 4.4272 cm

Collar outer diameter= 10.2565 cm.

<u>Second size.</u>

Cylinder inner diameter= 2.5450 cm.

Cylinder outer diameter= 3.2105 cm.

Collar inner diameter= 3.2105 cm.

Collar outer diameter= 10.2565 cm.

<u>Third size.</u>

Cylinder inner diameter= 4.4510 cm.

Cylinder outer diameter= 5.1165 cm.

Collar inner diameter= 5.1165 cm.

Collar outer diameter= 10.2565 cm.

The U-shape cut in each inserted cylinder has a height of 2.54 cm and a width of 1.91 cm. The cut in each collar has an inner width of 1.91 cm (corresponds to its inner diameter) and an outer one of 3.175 cm.

<u>Bronze leaf springs:</u> Each of them is 3.3325 cm long, 0.0127 cm thick, and has a width of 0.3175 cm. Hence, we can evaluate the constant of these springs, K , using the following expressions (Timoshenko and

Young,1968):

$$K=P/\delta=3EI/l^3$$

where E is the modulus of elasticity for tension, l is the length of the spring, and the moment of inertia, I , is given by the expression:

$$I=bh^3/12$$

with b being the width and h the thickness of the spring, respectively.The other symbols are defined in figure 13.

With E=14000000 psia , we find , K=4.24 N/m.

3.1.3.2. Operation.

In order to operate the system we need to put it in a strong magnetic field. The oscillation of the inner cylinder is induced by an alternating current. The alternating current is introduced by a source through wires attached to the copper shafts.

With the arrangement described previously the motion of the inner cylinder is not truly rectilinear, but it follows an arc determined by the length of the springs. However, for small enough amplitude of oscillation, the motion can be regarded as truly rectilinear, and the cylinder exhibits sinusoidal oscillation. The frequency of oscillation has to be high enough in order to approach flow conditions suitable for drag reduction, as will be explained later.

3.1.3.3. Electromagnetic field and electronic circuit.

The magnet consists of three movable coils, two iron cylinder poles and one U-shape yoke. A power supply for the coils is needed. The coils should be arranged in an appropriate position for maximum and homogeneous magnetic field strength at constant current supply. The average magnetic strength depends on the average distance between the two iron poles and the current through the coils. The gap should be about 14 cm, so that there is enough room for the flow system to be mounted.

The magnetic field strength can be measured by a Gauss meter (supplied by Boonton Electronics Corp., Randolph, NJ). The relation between magnetic strength and current through the coils can be found by performing a small experiment: We can measure the magnetic strength at center position for various values of the current going through the coils, and then plot the results of the measurements. A magnetic field strength of about 0.10-0.15 Wb/m^2 seems to be appropriate (Chang,1975; Bertelsen,1974). Then, the current can be found by the above experiment.

Power supplies are produced by Abacus Controls Inc., Sommerville, NJ, and magnets by Wayne Co., NJ.

Some electronic equipment is necessary to provide an alternating current for the oscillating cylinder. A block diagram of this equipment is shown in figure 14. The function generator (Global Specialties

Corp., CT) generates the sine wave and controls the frequency and amplitude of the alternating current. The power amplifier (Kepco Inc.,NY) amplifies the signal. The ammeter indicates the alternating current going through the oscillating cylinder (Sensitive Research Instruments, NY). The impedance transformer is a variable resistor (Enox Resistor Co., NY). A value of the current between 0.5 and 1 A should be suitable.

3.1.3.4. Test Fluids.

Two kinds of incompressible fluids are to be used in this experiment: Newtonian and non-Newtonian. Actually, we are primarily interested in the non-Newtonian fluids because they exhibit viscoelastic behaviour, which we expect to study. However, the Newtonian fluids play a very important role, as they can be used to compare with the results of the non-Newtonian fluids.

a. Newtonian fluids: A mixture of glycerine and water with composition of glycerine 50% per weight will be used. The reason for choosing this specific fluid is that the experimental results can be employed to confirm earlier works (Bertelsen et al,1973; Chang, 1975). This mixture has a density of 1.1235 g/ml and its refractive index is 1.3985 (both values correspond to room temperature). The method of preparation of this mixture is straightforward.

Bertelsen et al (1973) have used this mixture in an oscillating cylinder system for a value of the modified Reynolds number, R_s , of about 0.75, where $R_s = \omega s^2/\nu$, ω being the frequency and s the amplitude of oscillation and ν the kinematic viscosity of the fluid. For values of R_s between 90 and 400 they used pentane (with density 0.6262 g/ml and refractive index 1.3575, at room temperature).

Water is also an appropriate Newtonian fluid for our experiments.

b. Non-Newtonian fluids: Only polymers will be used at this stage. The reason is that these macromolecules have been extensively studied, and many data are available. The large number of polymers which are effective drag reducers makes the choice of the test fluids a difficult task.

Polyacrylamide and polyethylene oxide are certainly the most popular drag reducing polymers. Solutions of polyacrylamide (PAM) exhibit a highly elastic behaviour. Two kinds of PAM can be used: The one is a typical PAM under the commercial name Separan AP-30 (supplied by Dow Chemical Co.) or P-250 (supplied by American Cyanamid Co.). The other is a hydrolyzed high molecular weight and slightly anionic PAM. Its commercial name is Polyhall 295, and it is manufactured by Stein Hall Co.

Solutions of Separan AP-30 in glycerine-water mixture and distilled

water, and aqueous solutions of Polyhall 295 will be used. Since we are interested in studying the drag reducing behaviour of very dilute solutions, we want to test solutions of concentrations from 0 to 500 ppm per weight. Actually, a suitable range of concentrations is: 1,5,10,20,30,40,50,75,100,250,500 wppm. By choosing different kinds of PAM polymers we study the effect of the structure and the ionic character of this polymer on the results.

Very recently, Oliver and Bakhtiyarov (1983) used some anionic PAM (commercial names Magnafloc LT25 and Magnafloc E10) and showed that these polymers were effective drag reducers at concentrations of 0.1 wppm. But, for Separan MG-200, a PAM with low degree of hydrolysis (supplied by Dow), they observed drag reduction at 0.5 wppm. These polymers were dissolved in Birmingham tap water having pH=7.6 and containing basically chlorine,sodium,silicates and fluoride.

Rochefort et al (1984) used another partially hydrolyzed PAM, the Separan AP-273. The molecular weights of Separan AP-30, Separan MG-200 and Separan AP-273 are 3×10^6, 10×10^6, and 6×10^6, respectively. It is interesting to test in our system the Separan MG-200 polymer at concentrations below 1 wppm.

The preparation of PAM solutions is more difficult than that of the Newtonian fluids. PAM are supplied as white powders. The solution is obtained by adding the powder to the solvent under conditions of slow stirring, which has to be performed gradually and at room temperature.

The mixing and time conditions are very important, especially for the high molecular weight polymers, in order to avoid flocculation. The solutions of different concentrations are obtained from the more concentrated (here 500 wppm) by successive dilutions. More details about the preparation of polymer solutions are given by Davidson (1980).

The solutions described above are fresh. However, we are also interested in sheared solutions. The reason is that mechanical degradation plays an important role in drag reduction effectiveness, as mentioned previously (Chang and Darby,1983). So, the elastic properties of shear-degraded solutions of Separan AP-30 and Polyhall 295 at the concentration range mentioned above, will be measured.

The use of fresh PAM solutions will enable us to compare with the results of Chang and Schowalter (1979).

Aqueous polyethylene oxide (PEO) solutions are obtained by diluting polyox polymers in distilled water. We will use the same concentrations as in the case of PAM solutions. The method of preparation is similar to that used for the Separan solutions. The PEO in powder form is sprinkled uniformly over a large surface of distilled water to avoid clumping of particles. Solution takes place through diffusion at low temperature (about 5^0C) for a period of several days. Occasional stirring is needed to ensure adequate dispersion of the solute. The solution can be used at room temperature.

Typical PEO samples can be obtained from Union Carbide Corporation under different commercial names: WSR-205, WSR-301, WSR-1105 with viscosity average molecular weights 6×10^5, 333×10^4, and 10^6, respectively (Little and Ting,1976). Both fresh and shear-degraded solutions of PEO will be used.

The initial motivation for using xanthan gum as another test polymer in the oscillating cylinder experiments came from the very recent studies of Rochefort and Middleman (1985). According to them, the interest in xanthan gum came about because it appeared to have a combination of the desirable properties which characterize an additive as good drag reducer: High molecular weight, good shear stability, and it behaves as a semi-rigid rod-like polyelectrolyte. The rheology of aqueous solutions of xanthan gum was studied by Whitcomb and Macosko (1978). The study of the elastic properties of this polymer may provide some insight into the mechanism for drag reduction in semi-rigid polymer systems.

Typical commercial xanthan polymers are Galaxy XB (produced by General Mills Chemical Co.), Keltrol (produced by Kelco Co.), and Xanflood (produced by Exxon). Fresh solutions at the range of concentrations mentioned before can be prepared by dissolving the appropriate amount of powder (xanthan polymer) in distilled water, under stirring. After the polymer has gone into solution some glycerine is added to bring the solution up to the desired concentration. Usually the

solvent consists of 12.5% glycerine and 87.5% water. Salt solutions can be made by adding sodium chloride to the solvent to make it 0.5% w/v. It is good to use the solutions at room temperature within 8 hours of preparation in order to avoid biodegradation problems. It is also interesting to study the rheological properties of shear-degraded xanthan solutions in our experimental system.

Fresh aqueous solutions of guar gum, a shear stable drag reducing agent, will be tested in the oscillating cylinder apparatus. A typical commercial guar polymer is produced by Stein Hall Company and is available under the name J2S1. The preparation of the solution requires addition of the appropriate amount of the polymer to the solvent (distilled water). First, the polymer is allowed to dissolve without agitation. Next, the solution is agitated gently by swirling, and more water can be added. It is important to avoid excessive agitation to prevent mechanical degradation. More details about the preparation, as well as some rheological studies of the aqueous guar solutions are available elsewhere (Kenis,1971; Whitcomb et al,1980). The biodegradation of these solutions starts within 8 hours of their preparation, so their applicability to drag reduction is limited. Deshmukh et al (1985) have shown that purification of guar gum enhances both drag reduction effectiveness and biodegradation resistance. Commercial guar gum can be purified by the method of Whitcomb et al (1980). It is evident, therefore, that the study of the rheological

behaviour of the purified guar solutions may be useful in gaining a better understanding of the mechanism of drag reduction by these additives.

Finally, it is interesting to study the behaviour of dilute solutions of polystyrene (which is a relatively flexible, linear polymer) in our system, in order to compare with parallel birefrigence studies done with the same polymer (Fuller and Leal,1981; Leal,1985. See also section 3.2.3.). These solutions can be either neutral polystyrene or polyelectrolyte solutions, like the Na^+ salt of polystyrene sulphonate, so that we can study the effects of salts on the dynamic properties (Miles et al,1983).

3.1.3.5. Characterization of the fluids.

The liquid viscosity and normal stresses can be measured in the Rheometrics System IV rheometer (Rheometrics Inc., Piscataway, NJ) using a cone-and-plate geometry. These viscometric properties are expressed as functions of shear rate. Details about the cone-and-plate geometry and appropriate expressions for the calculation of viscosity and shear and normal stresses are given by Schowalter (1978).

Chang and Schowalter (1979) used a Weissenberg R-16 Rheogoniometer and reported some difficulties in obtaining normal stress data for the very dilute solutions of Separan AP-30 (below 100 wppm). They were able,

however, to overcome this problem by using the data of Darby (1970), who modified the rheogoniometer in order to obtain results for these solutions. Also, Tanner (1970) proposed other techniques for the measurement of normal stresses in such cases.

There are many data available in the literature which can be used to confirm our experiments. Kuo and Tanner (1974) measured shear and normal stresses over a wide range of shear rates for aqueous solutions of Separan AP-30, Polyhall 295, WSR-301, PAM J-100, and solutions of polyisobutadiene in cetane. Argumedo et al (1978) obtained results for Separan AP-273 solutions in water, at concentrations above 120 wppm. They measured both viscosity and normal stresses.

Viscosity and primary normal stress difference data obtained in Rheometrics System IV are available for Separan AP-30 solutions (at concentrations above 300 wppm), hydroxyethylcellulose solutions (above 1000 wppm), xanthan solutions (above 1000 wppm), at a shear rate range from 1 s^{-1} to 1000 s^{-1}, and for 50 wppm hydroxypropyl guar solution for shear rates from 0.1 s^{-1} to 1000 s^{-1} (Collias,1986). All solutions tested were aqueous.

3.1.3.6. Velocity measurement.

The most critical and difficult part of the experimental work is the measurement of the fluid secondary velocity profiles around the

oscillating cylinder. Fluid mechanics researchers have used three major techniques to measure these velocity profiles: Mechanical probes, flow visualization technique and lasers.

The use of mechanical probes (e.g. total pressure probes or hot wire anemometers) is the conventional way of measuring local velocities. But, it disturbs -although to a small scale- the flow field, since one has to insert the velocity sensitive probes in the flowing fluid. This affects the accuracy of the measurement significantly, especially in the case of viscoelastic fluids.

Flow visualization techniques do not disturb the flow field as much as the mechanical probes. There are actually two such techniques: In the first, one observes the physical variations caused by pressure,temperature or density changes. In the second, one adds tracer particles or dyes into the flowing fluid, and by assuming that these materials follow the streamlines of the velocity field, one can obtain the velocity profile if the materials are visible to a camera or eye. This method is discussed in detail by Chang (1975).

Laser Doppler Anemometry or Velocimetry (LDA or LDV) is a non-invasive optical technique for measuring the fluid velocities by detecting the Doppler frequency shift of coherent light that has been scattered by small particles moving with the velocity of the fluid. This method has substantial advantages over the other techniques in flow situations where a non-invasive and accurate measurement is required.

The major advantages of LDA are its ability to measure one or more velocity components, its good spatial resolution and its independence from the thermophysical properties of the fluid.

Among the drawbacks of this method, the most severe are the following: Optical equipment is sometimes sensitive to vibrations, and frequency analyzers are not suitable for applications,with significant noise and extraneous radio-frequency signals. Also, sometimes the intensity of the light scattered is so weak, that it is very difficult to analyze the resulting noisy signals.

Due to the tremendous interest in LDA and its applications, numerous papers have been published, the first of which appeared in 1964 by Yeh and Cummins, who reported results of the measurement of fluid velocities in laminar pipe flow of water. The basic theory of LDA and some specific applications are well presented by Adrian (1984) and Durst et al (1981).

It is therefore clear, that LDA is undoubtedly the most popular application of lasers for the measurement of fluid velocities.

Another important application is the Laser Speckle Photographic technique (LSP), which when applied in fluid mechanics is also named Particle Image Velocimetry (PIV). This method uses the scattered light from the interior of a suitably seeded fluid, which is illuminated by a coherent beam from a pulse laser. The resulting speckle pattern can be photographed on high resolution film. A doubly exposed photograph of the

correlated speckle patterns produced by fluid dynamic motion contains all the information necessary to describe the motion throughout a selected plane. The advantages of LSP are: A low-power low-cost laser can be used for any velocity measurement. The speckle size may be adjusted to suit the resolution of the most convenient detector while still retaining information about displacements on an interferometric scale if required. It is also a promising method for investigations of non-viscometric flows of viscoelastic fluids, although this area has not yet been developed (Binnington et al,1983). The major disadvantage of LSP is the use of a photograph, leading to some loss in accuracy. More details about the principles of LSP and its applications are available in the literature (Baker et al,1980; Pickering and Halliwell,1984; Barker and Fourney,1977).

Very recently, Grandke (1985) has introduced the laser shadow technique for the investigation of turbulent flow. This technique, however, is only applicable if density variations exist, in order to obtain the shadowgraphs.

The choice of the appropriate technique for a specific measurement depends on many factors such as cost,accuracy,operational procedure and collection of data.

We have decided to use the LDA technique in order to obtain highly accurate measurements of the steady secondary velocity profiles. However, there are some problems to be encountered. The first one is

that the flow system should be such that it can be moved in any direction when the optical system is fixed, or vise versa, in order to measure the velocity profile of the whole flow field. The second problem is, as mentioned before, the elimination of vibrations. We can overcome this problem by mounting the flow system on an anti-vibrating table.

If the plane of the incident laser beams is vertical to the cylinder axis (horizontal), then the beams will have to cross the wall surface of both inserted cylinder and container. It is good to avoid this case because the laser light has to pass through four curved surfaces, with imperfect curvature, of course. Instead, we will use the laser in such a position, that the incident beams are in the same plane as the cylinder axis, say z.

We have decided to use forward scattering, which gives a stronger signal than backscattering and is, therefore, recommended for the measurement of very low velocities.

The measurement of the velocities can be accomplished in two modes: In the first, the laser beams cross at a certain point in the flow cell, forming an angle α. The velocity vector is in a plane vertical to that of the beams (the horizontal plane) and it is vertical to the bisection line of α. This is actually the first component, say v_1. In the second mode we rotate the plane of beams 90^0 around the cylinder axis (we can do that with the beam splitter) and we get similarily the other velocity component, say v_2. The total velocity vector is the sum of these two

vectors. We can decompose this vector in two other components (radial and angular), as shown graphically in figure 15. The steady secondary flow consists of these two velocity components. Both are functions of radial position and angular distance from the direction of oscillation.

Now, we recall that both the top and bottom enclosures of the flow cell consist of glass. This will facilitate the operation of LDA.

The problem of the flexibility of the flow system to move in any direction can be solved by mounting the system on the anti-vibrating table in such a way that it can rotate around its center axis.

The next problem is how to distinguish primary and secondary flow. Actually, the laser measures the "combined" velocity resulting from both flows, so we need to subtract the primary velocity. This is, however, not easy, because the velocities differ by two orders of magnitude (Bertelsen, 1974) and if we cannot measure both with the same accuracy, then we might loose in accuracy in our results. Also, we were told from TSI people (TSI Inc., St.Paul, MN) that the decomposition in primary and secondary velocities is not recommended because it causes problems in the operation of the laser, related to the frequencies of the signal processor. The solution to the problem comes from the observation that primary flow is oscillatory and it becomes zero at the maximum amplitude of oscillation. If, therefore, we measure the velocity at the time corresponding to maximum amplitude, the net measurement is the secondary velocity. There are still some problems, however, due to the low

secondary velocities: The signal processors by TSI start at a frequency of 1 kHz and go up to 150 MHz. It is found that for a velocity value of 0.12 cm/s the Doppler frequency is 1 kHz, compatible with the signal processor, and one can get the signal. However, for velocities below 0.12 cm/s we have to use frequency shifters (Bragg cells). These can cause a frequency shift of 2 kHz, enabling the laser signal to be processed. Specifically, for a velocity of 0.1 cm/s the Doppler frequency is 860 Hz. With the Bragg cells the frequency becomes either 2860 Hz or 1140 Hz, and so, we can get signal in both cases. The Bragg cell will also enable us to account for the direction of the secondary flow. When we go from left to right in this example, the frequency is 2869 Hz, and when we go from right to left it is 1140 Hz.

The difficult problem in this approach is how to perform measurements at the positions of zero primary flow. The one way to overcome this problem is by using a chopper disk, which is such that the laser beams cross at a point in the flow cell only when the amplitude of oscillation is maximum. This requires different disks or different rotational speed of the disk ,for different primary frequencies, what is hard to accomplish. An alternative way is to take advantage of the fact that the signal processor has an inhibit line , i.e. it can stop from taking data. So, one has to make it to take data only when the primary velocity is zero. Also, one can take all the velocity data and then keep only these corresponding to maximum amplitude of oscillation.

Recently, we came out with the idea of "time averaging", which seems to be the simplest and more promising for our application. This idea is based on the fact that the long-time average of a constant-frequency periodic motion is zero. Thus, by taking the average of the "combined velocity" (superposition of periodic primary and steady secondary velocity) over a long time period, we end up with the steady secondary velocity only. The results of some preliminary experiments (order of magnitude estimates of the steady secondary velocities) are encouraging.

The amplitude of oscillation can be satisfactorily measured by using either a high speed camera or a fibre-optic coupled displacement sensor (Jones,1986). The center positions of the steady secondary flow can be determined with the laser system.

Another important point is the use of light scattering particles, which are essential for the creation of the scattered light. We have decided to use TiO_2 particles, which are considered ideal for their refractive index, and also satisfy the "rule of thumb", which says that the particle diameter should be 3-5 times less than the fringe spacing (TSI,1983).

A final problem is the calibration of the laser. The position can be easily calibrated using thermistors, which are temperature sensitive semiconductors. When the laser beams cross on one of them, its temperature increases enormously and so, knowing its position, we know where the beams cross. The velocity calibration is harder since there is

no point in the flow cell with a-priori known velocity. We are still working in this problem and we believe that by following the known motion of the inner cylinder we might find a way to calibrate for velocity. The optical arrangements for the LDA studies are shown in figure 16.

3.1.3.7. Experimental procedure and expected investigations.

The inner cylinder is positioned vertically and at the center line of the flow cell. By adding the test fluid in the gap between this cylinder and the outer (inserted) one, and by introducing an alternating current through the wires, we can observe the steady secondary flow induced by the oscillating cylinder.

The experiments are to be performed at room temperature and there is no need for a specific temperature control system since it was found that, for such a system, the time needed to raise the fluid temperature by $1^{\circ}C$ by the heat generated from the magnetic coils was about 1 hour (Chang, 1975).

Our goal is to interpret the results of the measurements of the steady secondary velocity profile described in the previous section. It can be shown (Raney et al, 1954) that at $\theta=45^{\circ}$, $u=0$, where u is the radial velocity (note that υ is the angular velocity). So, the measurements of the secondary velocity at $\theta=45^{\circ}$ give us directly the

value of u as function of the radial position. It is also convenient to take measurements at various radial positions along $\theta=90°$ or $\theta=0°$, because then $\upsilon=0$.

The plots of angular and radial velocity can be obtained as functions of r/a, r being the radial position and a the radius of the inner cylinder. These plots can be compared with theoretical predictions (best fit to the data) to examine the relative agreement between theory and experiments. They can also be compared with some previous results (Chang,1975). Also, by comparing secondary velocity profiles of different fluids at various concentrations we can get an idea of how these parameters influence the results. It is also true that different test fluids correspond to different macromolecular behaviour in the primary flow and, therefore, result in different secondary flow.

The characterization of the nature of the steady secondary flow can be made by examining the center positions of the steady secondary circulations. More specifically, these center positions can be determined as function of A/a, where A is radius of the outer cylinder. The data points to be obtained will be fit with theoretical predictions resulting in the determination of the relaxation time for the test fluid by the best fit to the data. Thus, an indirect method can be used for the determination of the elastic properties of the drag reducing additives.

It is obvious from the above development, that the frequency of oscillation plays a very important role in the behaviour of the test fluid. In fact, we want to reach high frequencies up to about 2 kHz, so that we have rapid and unsteady shearing in the primary flow field. At this point it should be noted that experiments on the acoustic streaming in liquids from vibrating bodies over a wide range of frequencies have been made by Ghabrial and Richardson (1955). Since the characteristics of the steady secondary flow will depend on the behaviour of the polymer molecules in the primary flow (i.e. the molecular stretching), at different frequencies we expect different amounts of stretching and, therefore, different characteristics of the secondary flow. We recall that by using this oscillating cylinder system we try to approximate a situation of turbulent flow since we have an organized, unsteady and high frequency deterministic primary flow.

In conclusion, the primary flow is a well defined time-dependent flow in which the macromolecules of the dilute drag reducing solutions stretch, and the resulting steady secondary flow provides a tool for characterizing these solutions.

Since the secondary flow is extremely sensitive to small amounts of elasticity (Chang and Schowalter, 1979), this method can be effectively be used to ascertain relative degrees of elasticity even in very dilute polymer solutions.

Based on the qualitative results of Chang and Schowalter (1974) we can study the effect of elasticity of the solution on flow reversal. The experimental streamlines of the steady secondary flow can be compared with the corresponding best fit streamlines in order to test for the accuracy of the experiments. The previous qualitative work will be extended to account for the effect of the other test fluids to be used on the steady secondary flow patterns.

So, our experimental studies will provide new diagnostic tools for studying the flow-induced stretching of macromolecules in dilute solution, and give some insight into the mechanism of drag reduction by polymers.

3.1.4. Theoretical development.

The mathematical formulation of the problem is described elsewhere (Chang and Schowalter, 1979). Here we just summarize the important points and focus on the problems involved with the choice of constitutive equations.

By using cylindrical coordinates for which the z-axis is coincident with the central axis of the oscillating cylinder, the equations of motion and continuity for two-dimensional fluid motion give:

r-Momentum:

$\rho[(\partial u/\partial t)+u(\partial u/\partial r)+(\upsilon/r)(\partial u/\partial\theta)-\upsilon^2/r]=$

$$-(\partial P/\partial r)+(1/r)[(\partial/\partial r)(r\tau_{rr})]+(1/r)[(\partial/\partial\theta)(\tau_{r\theta})]-\tau_{\theta\theta}/r$$

θ-Momentum:

$$\rho[(\partial\upsilon/\partial t)+u(\partial\upsilon/\partial r)+(\upsilon/r)(\partial\upsilon/\partial\theta)+u\upsilon/r]=$$

$$-(1/r)(\partial P/\partial\theta)+(1/r^2)[(\partial/\partial r)(r^2\tau_{r\theta})]+(1/r)[(\partial/\partial\theta)(\tau_{\theta\theta})]$$

Continuity:

$$\partial u/\partial r+u/r+(1/r)(\partial\upsilon/\partial\theta)=0$$

The dependent variables can be expanded in a small parameter $\delta=s/a$, where s refers to the amplitude of oscillation. So, we have a cylinder executing small amplitude oscillations:

$$u=\delta u_0 e^{-i\omega t}+\delta^2(u_s+u_2 e^{-2i\omega t})+\ldots$$

$$\upsilon=\delta\upsilon_0 e^{-i\omega t}+\delta^2(\upsilon_s+\upsilon_2 e^{-2i\omega t})+\ldots$$

$$P=\delta P_0 e^{-i\omega t}+\delta^2(P_s+P_2 e^{-2i\omega t})+\ldots$$

$$\tau_{rr}=\delta\tau_{rr}^{(0)}e^{-i\omega t}+\delta^2(\tau_{rr}^{(s)}+\tau_{rr}^{(2)}e^{-2i\omega t})+\ldots$$

$$\tau_{\theta\theta}=\delta\tau_{\theta\theta}^{(0)}e^{-i\omega t}+\delta^2(\tau_{\theta\theta}^{(s)}+\tau_{\theta\theta}^{(2)}e^{-2i\omega t})+\ldots$$

$$\tau_{r\theta}=\delta\tau_{r\theta}^{(0)}e^{-i\omega t}+\delta^2(\tau_{r\theta}^{(s)}+\tau_{r\theta}^{(2)}e^{-2i\omega t})+\ldots$$

With respect to a laboratory coordinate system, the inner cylinder oscillates with velocity $U=U_0 e^{-i\omega t}$.

For the boundary conditions it is convenient to consider the coordinate system fixed to the inner cylinder, while the concentric outer cylinder is forced to oscillate perpendicular to the axis of the cylinder. Thus, we have:

$$u=\upsilon=0 \quad \text{at } r=a$$

$$u(A,\theta,t)=U_0\delta\cos\theta e^{-i\omega t}-(i/\omega)(\delta U\cdot\nabla v)\cdot e_r \quad \text{at } r=A$$

$$\upsilon(A,\theta,t)=-U_0\delta\sin\theta e^{-i\omega t}-(i/\omega)(\delta U\bullet\nabla v)\bullet e_\theta \quad \text{at } r=A$$

where e_r and e_θ are unit vectors in the r and θ direction, respectively, and v is the velocity of a material point in the outer cylinder (Chang and Schowalter,1979).

The next step is to couple the equations of continuity and motion with an appropriate constitutive equation, and solve the system to find the primary (order δ) and the secondary (steady terms of order δ^2) velocity profiles and the effect of elasticity on flow pattern.

Choice of constitutive equations.

This is a difficult task. One has to use a fluid model which is neither too simple (doesn't describe adequately the flow situation), nor too complicated (it is very hard or even impossible to solve it, at least analytically).

As a first approach it is convenient to use a three parameter Oldroyd constitutive equation. This is a constitutive equation of the differential type (Schowalter,1978; Bird et al,1977a):

$$T+\lambda_1(\Delta/\Delta t(T))=2\mu_0[D+\lambda_2(\Delta/\Delta t(D))]$$

$$S=-pI+T$$

where T is the extra stress tensor, Δ the Jaumann derivative, S the stress tensor, p an arbitrary isotropic pressure and D the rate-of-deformation tensor:

$$D=(1/2)[\nabla\upsilon+(\nabla\upsilon)^\tau] \ .$$

The three parameters characterizing the fluid are the zero-shear viscosity, μ_0, the relaxation time, λ_1, and the retardation time, λ_2. The Jaumann derivative is defined as:

$$\Delta T_{ij}/\Delta t = \partial T_{ij}/\partial t + \upsilon^k T_{ij,k} - \Omega_i^k T_{kj} - \Omega_j^k T_{ik}$$

Here, Ω is the vorticity tensor, defined as:

$$\Omega_{ij} = (1/2)(\upsilon_{i,j} - \upsilon_{j,i}) \ .$$

The reason for starting with this particular constitutive model is that it is relatively simple. Also, we can compare the results with the previous work of Chang and Schowalter (1976,1979).

Our aim is, however, to employ fluid models which describe more accurately the behaviour of dilute polymer solutions (Bird et al,1977b). We are currently working on the subject, and at present no choice has been made of models suitable for our problem. Integral constitutive equations in a Goddard expansion form (Bird et al,1974) may be applicable to our problem. Other suitable constitutive models for dilute polymer solutions are described by Tanner (1985). However, we are currently focusing on the work of Giesekus (1985), who has developed general constitutive equations for polymer fluids based on the concept of configuration-dependent molecular mobility. One major advantage of the models proposed by Giesekus is that they are general, and, by adjusting their parameters, one can obtain simpler and well known fluid models.

The constitutive model developed by Phan-Thien et al (1984) seems to

be promising for dilute polymer solutions, and might be useful in our case. It is an elastic dumbbell model with a nonlinear spring and conformation-dependent hydrodynamic properties. Also, the freely jointed model applied to dilute solutions (Bird,1982) is an interesting one. Armstrong and Ishikava (1980) investigated the rheology of dilute solutions of flexible macromolecules idealized as nearly-Hookean dumbbells, and the constitutive equation they developed may prove to be valuable to us. Recently, Piau and Doremus (1984) presented a constitutive equation for dilute polymer solutions in strong elongational flow. They claimed that their model describes well the important effects that appear in strong flows. These effects are explicitly related to two mechanisms generating important elongational stress, one being a viscous dissipation by hydrodynamic interaction, and the other a macromolecular deformation. They also speculated that another advantage of this model is its relative simplicity. Finally, the work of Tanner (1973), who developed a model for dilute solutions considering the bead-filament dumbbell molecule, may be helpful in our search for appropriate constitutive equations for our problem.

3.2. Future work.

The first task is to continue and complete the on-going work described earlier. We have to set up the experimental apparatus and run the experiments. At the same time the theoretical part should be

developed with the use of appropriate constitutive equations as discussed before. Once results (both theoretical and experimental) are available, we can extend this work to other areas.

3.2.1. Characterization of drag reducing surfactant systems.

The problem of rheological characterization of dilute solutions of surfactants,exhibiting drag reducing behaviour, is of great interest. We hope to test some surfactant systems in the "oscillating cylinder viscometer". Such systems are the dilute aqueous solutions of the cationic surfactants alkyltrimethylammonium- and alkylpyridinium- salicytates, which consist of rod-like micelles. Alkyl chain lengths of these soaps can be of 10,12,14,16 or 20 carbon atoms. We can have for example, n-dodecyltrimethylammonium-, n-tetradecyltrimethylammonium-, n-hexadecyltrimethylammonium- and n-hexadecylpyridinium- salicytates. The reason for choosing these systems is that there are some data for their rheological properties available in the literature (Hoffmann et al,1984; Elson and Garside,1983; Bewersdorff and Ohlendorf,1985).

Our hope is to investigate the drag reducing behaviour of these solutions. Since they exhibit viscoelasticity, their behaviour in unsteady non-viscometric flows could be related in a sense to that of dilute polymer solutions. The first step is basically qualitative. We want to study the nature of the steady secondary flow of such solutions over a wide range of concentrations. As in the case of polymers, we

expect to find the concentration corresponding to the transition from non-Newtonian to Newtonian behaviour. Also, the differences in the secondary flow patterns of Newtonian and surfactant solutions will give us useful information about the effect of elasticity of surfactants on this flow. A comparison will be made between the elastic properties of polymer and surfactant solutions.

In the second step the approach will be quantitative. We expect to measure the steady secondary velocity profiles as in the the case of polymers, and thus determine relaxation times by combining experimental results and theoretical predictions. The main problem is that there are no constitutive equations for surfactants available. We expect, however, to be able to overcome this difficulty by using appropriate polymer constitutive models which approximate the behaviour of the surfactant solutions.

If the oscillating cylinder system proves to be a good method for the characterization of the drag reducing surfactant solutions, it might be interesting to relate the results with the conventional method of characterizing their viscoelasticity, the Swirl Decay Time.

3.2.2. Systematic studies of the effect of molecular parameters on the viscoelastic properties of the drag reducing additives.

So far we have been concerned with test fluids of different

molecular weights, concentrations and ionic character. There are, however, more molecular parameters which can be related to the macromolecular stretching and, therefore, to the drag reducing properties of the additives. Such parameters are the molecular weight distribution, the molecular structure (e.g. the degree of side chain branching or the level of "backbone" stiffness), the pH of the solvent and other features which may alter the solvent-solute interaction at constant temperature. It is interesting to study the effect of these parameters on the elastic properties of the test fluids.

Another motivation for further work is the fairly good drag reducing performance of nonionic surfactants. An attempt will be made to use polyethylene alcohol surfactants like Neodol 23-6.5, Neodol 25-7 and Neodol 45-7 (supplied by Shell Chemical Co.). These additives can be easily dissolved in water to form aqueous solutions.

It has been observed that by adding glycerine in aqueous solutions of PEO one can increase the solution viscosity. Obviously, there are many different substances which can alter the viscosity of a given polymer solution at constant temperature. This proves to be a motivation for studying the effect of solvent's viscosity on the elastic properties of the solution or comparing the elastic properties of solutions of the same macromolecule in different solvents.

Another modification of drag reducing solutions can be made by using solutions of mixtures of polymers, as discussed in earlier sections of

this work.

Hydroxyethyl cellulose (HEC) is a water-soluble polymer yielding high drag reduction (Meter,1964). Recently, a research group from Hercules Company changed the structure of this polymer by adding sodium oleate, and produced the so-called hydrophobically modified hydroxyethyl cellulose (HMHEC). The study of this modified polymer revealed unique rheological properties due to the polymer-surfactant interactions (Gelman,1985). It will be interesting to extend these studies by measuring the elastic properties of dilute solutions of HMHEC and comparing with the case of HEC. So, we may gain a better understanding of how the molecular structure of HMHEC influences its rheological behaviour.

In order to investigate the effect of the structure of a surfactant solution on its drag reducing behaviour we can test mixtures of the cationic surfactants mentioned before with some salts (e.g. NaCl, NaBr, Na-salicylate) and the nonionic with some electrolyte (e.g. $Na_2S_2O_3$).

3.2.3. Relation to flow birefrigence studies.

The flow-induced stretching of macromolecules in dilute solution has been extensively studied both theoretically and experimentally (Fuller and Leal,1980; Leal et al,1980). The birefrigence method has been proved to be a useful tool for studying conformation changes in a polymer

solution due to the presence of flow (Macosko,1984). It is one of the most commonly used methods to study the dynamics of polymer molecules in dilute solution (Zimm,1956; Leal,1984,1985). It can also be used to account for the effect of molecular parameters on the drag reducing properties of these solutions (Scrivener et al,1979).

We believe that by performing flow birefrigence experiments, using the test fluids characterized in the oscillating cylinder system, we may be able to test our earlier work. Also, since both methods (oscillating cylinder and birefrigence) deal with the study of deformation of macromolecules, their combination may provide an understanding of molecular stretching and its relation to drag reduction.

3.2.4. Channel flow studies.

The ultimate goal of this work is to test the results of the characterization of the additives under drag reducing flow conditions. More precisely, the studies of the oscillating cylinder system allow us to make a comparative ranking of the drag reducing additives. We expect to test these additives in turbulent channel flow by measuring the drag reduction and, then, comparing their effectiveness. These channel flow studies will be a practical application of our work on rheological characterization of dilute drag reducing solutions and, also, a reliability test for our results.

The measurement of mean velocity profile, turbulence intensities and other turbulent flow characteristics, if needed, will be performed with a two-color LDA system (Adrian,1984; TSI,1983).
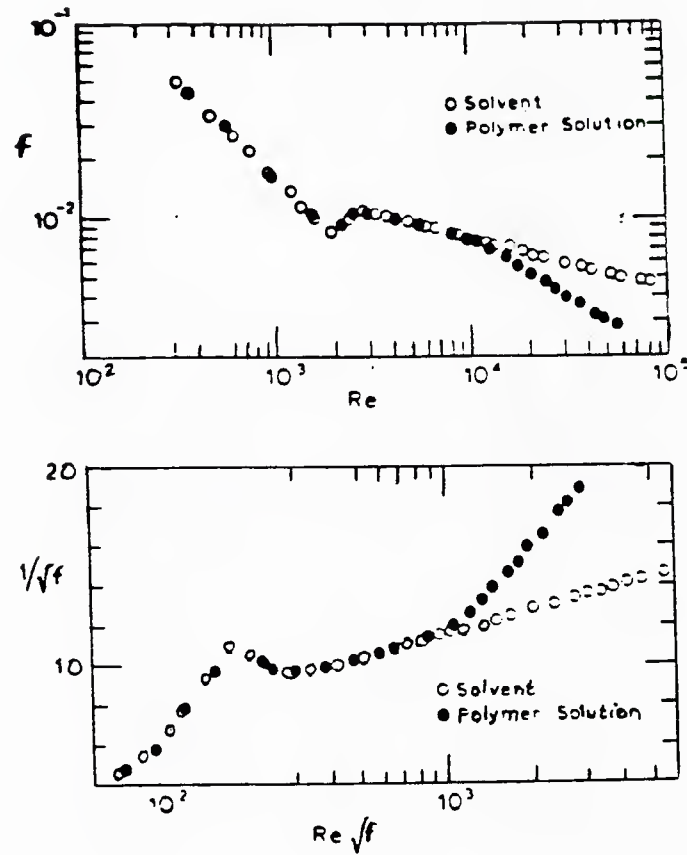
Figure 1: Drag reduction depicted on various gross flow coordinates. f: Friction factor, Re: Reynolds number, Polymer solution: PEO in distilled water at concentration 296 wppm (from Virk (1975a)).
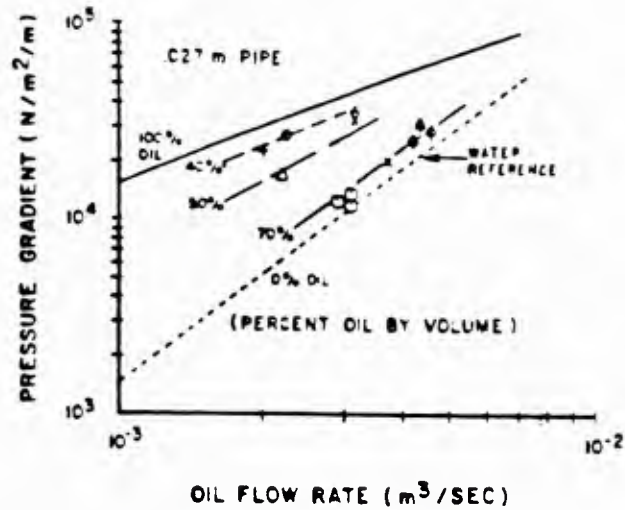
Figure 2: Drag reduction for white mineral oil-water systems at different compositions (from Sifferman and Greenkorn (1981)).
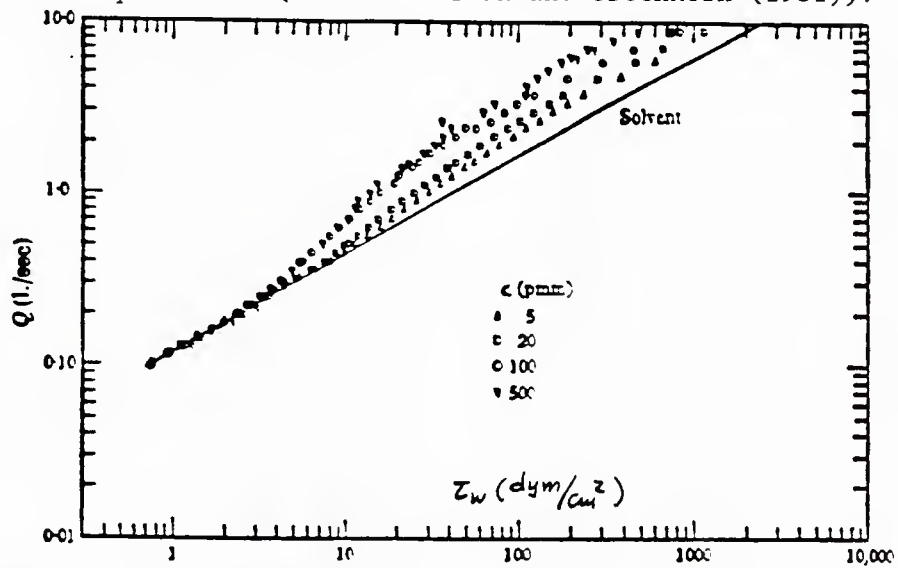
Figure 3: Typical flow diagram for drag reduction in aqueous PEO solutions. Q: Flow rate, τ_w: Wall shear stress (from Virk et al (1967)).
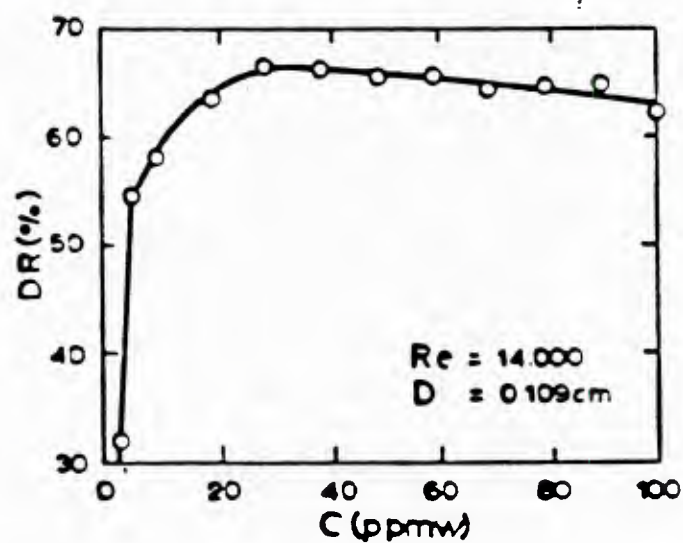
Figure 4: Drag reduction in turbulent pipe flow of aqueous PEO solutions. DR(%): Percent drag reduction, C: concentration (wppm), D: Pipe diameter (from Hoyt (1972)).
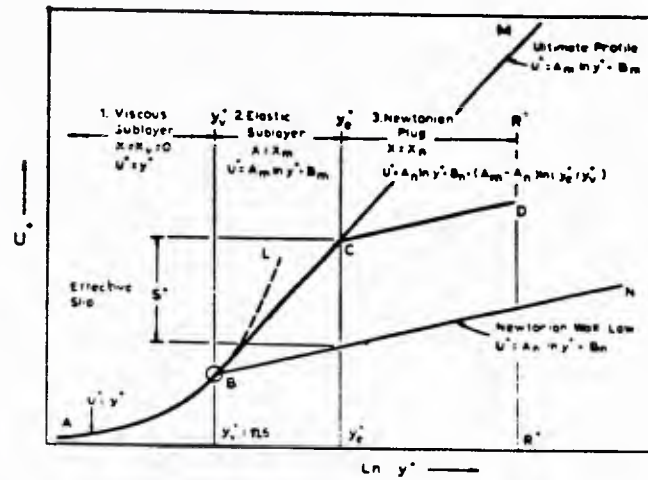
Figure 5: Mean velocity profiles during drag reduction. U^+ and y^+ : Normalized local mean velocity and azimuthal direction from the origin of the pipe wall, respectively. Subscripts e and υ refer to the outer edge of the elastic sublayer and the outer edge of the viscous sublayer, respectively (from Virk (1975a)).
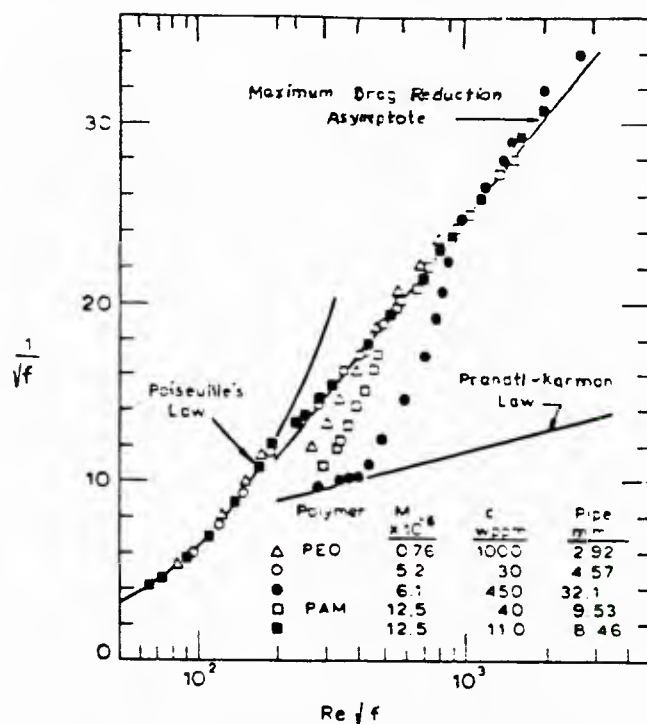
Figure 6: Gross flow trajectories exhibiting maximum drag reduction (from Virk (1975a)).
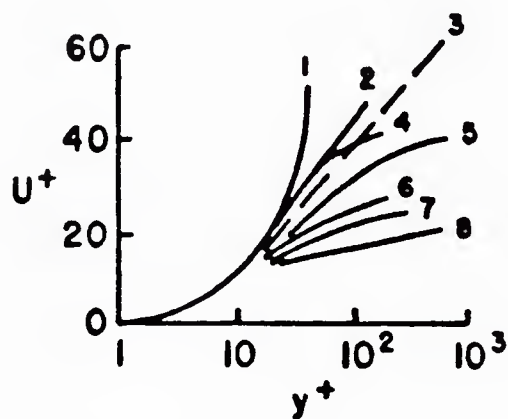
Figure 7: Sketch of representative pipe mean flow velocity profiles for various experimental studies. The dashed line is the Virk's Maximum Drag Reduction Asymptote (from Lumley and Kubo (1984)).
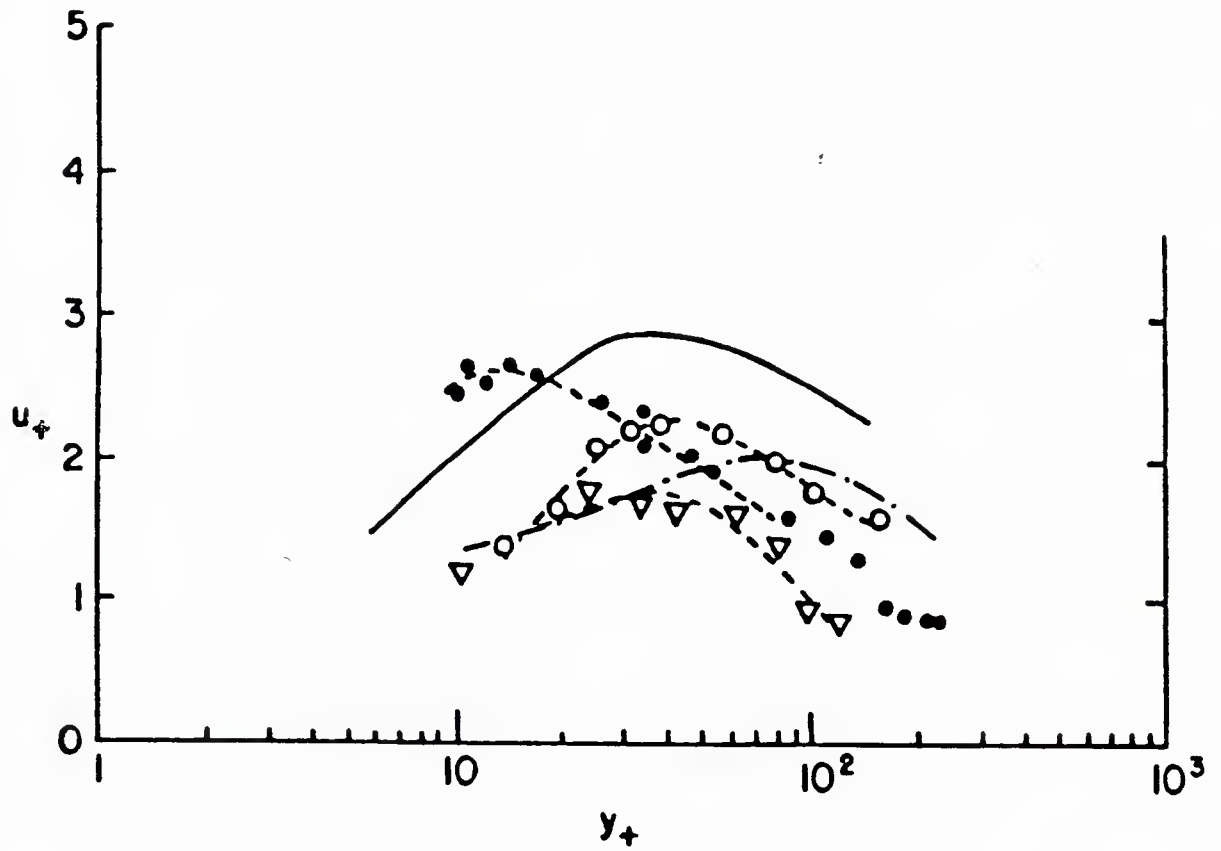
Figure 8: Representative turbulent intensity distributions (from Kubo and Lumley (1980)).

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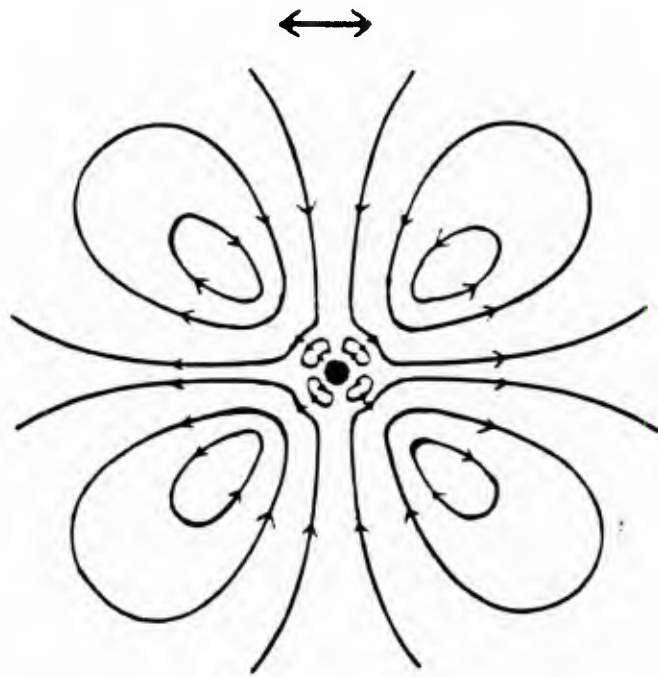
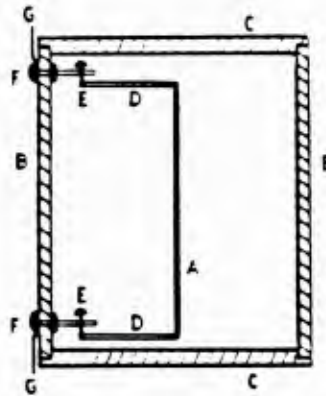**Figure** 9: Steady secondary flow for Newtonian fluid (from Chang and Schowalter (1974)).
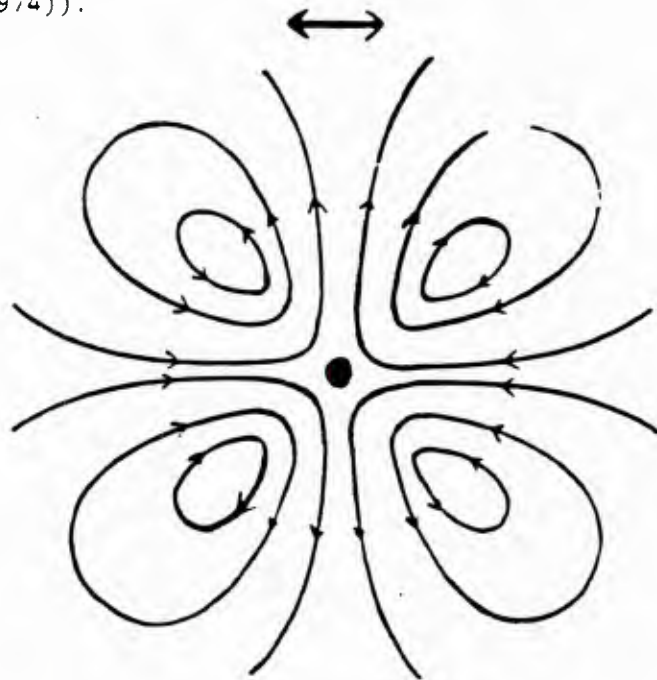
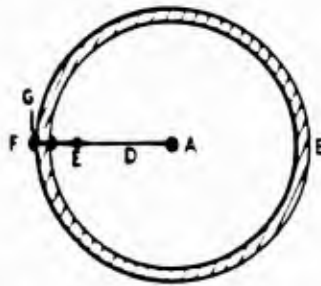**Figure** 10: Steady secondary flow for viscoelastic fluid (from Chang and Schowalter (1974)).

Figure 11: Flow system (a: Side view, b: Top view)
A: Inner cylinder, B: Container wall, C: Enclosures, D: Springs, E: Movable connections, F: Cooper shafts, G: Wires for alternating current. (From Chang and Schowalter (1979)).
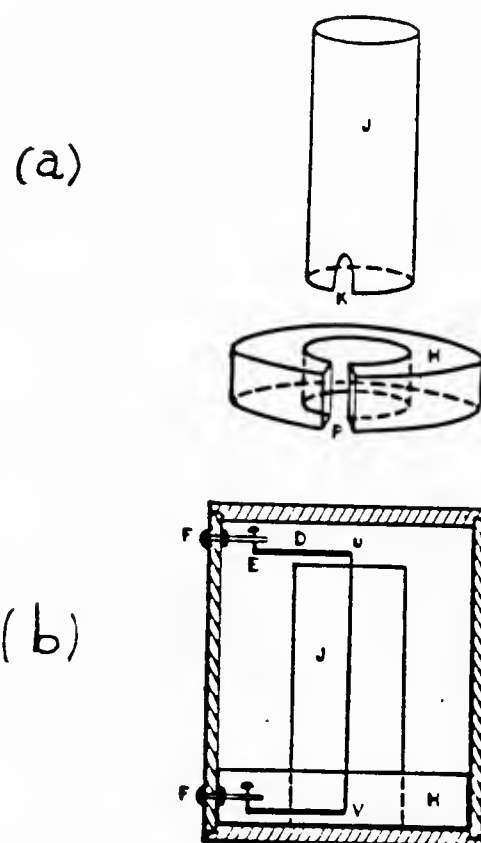
Figure 12: Inserted cylinder system (a: Inserted cylinder and collar, b: Flow system with inserted cylinder).

K: U-shape cut, J: Inserted cylinder, H: Collar, P: Cut of collar. (From Chang and Schowalter (1979)).
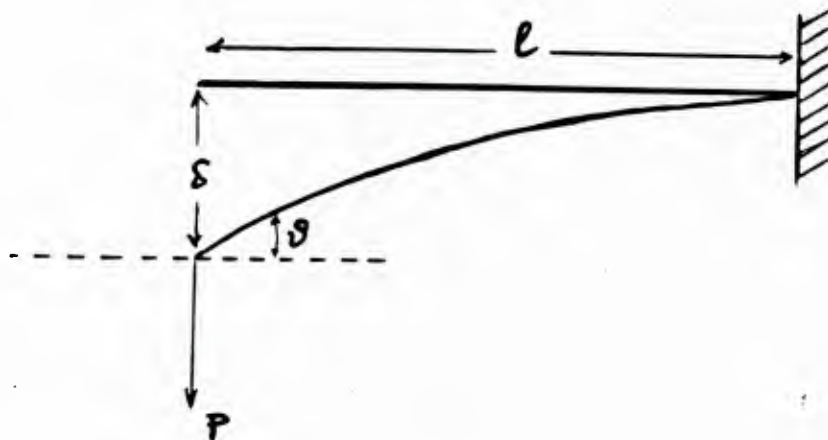
Figure 13:

Determination of spring constant.

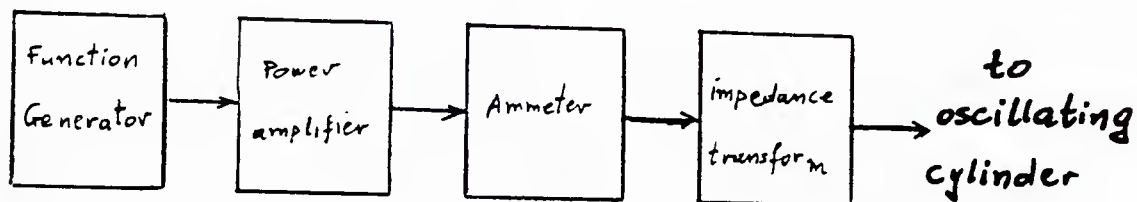δ: Deflection of the beam, ϑ: Slope, P: Load, l: length of the beam at rest.

Figure 14:

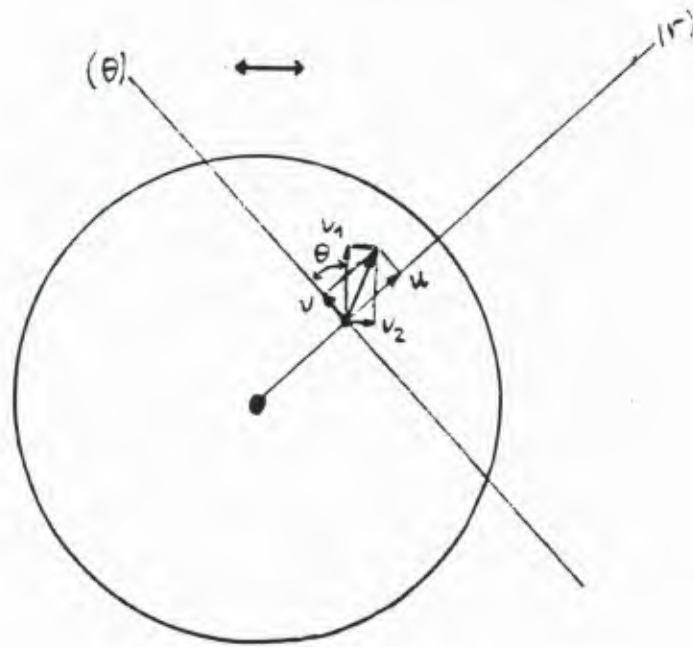Block diagram for the electronics.

Top view of the flow system

Figure 15: Decomposition of velocity in angular and radial components.

photomultiplier tube

Lenses

Flow system

lenses

beam separator

Bragg cells

beam splitter
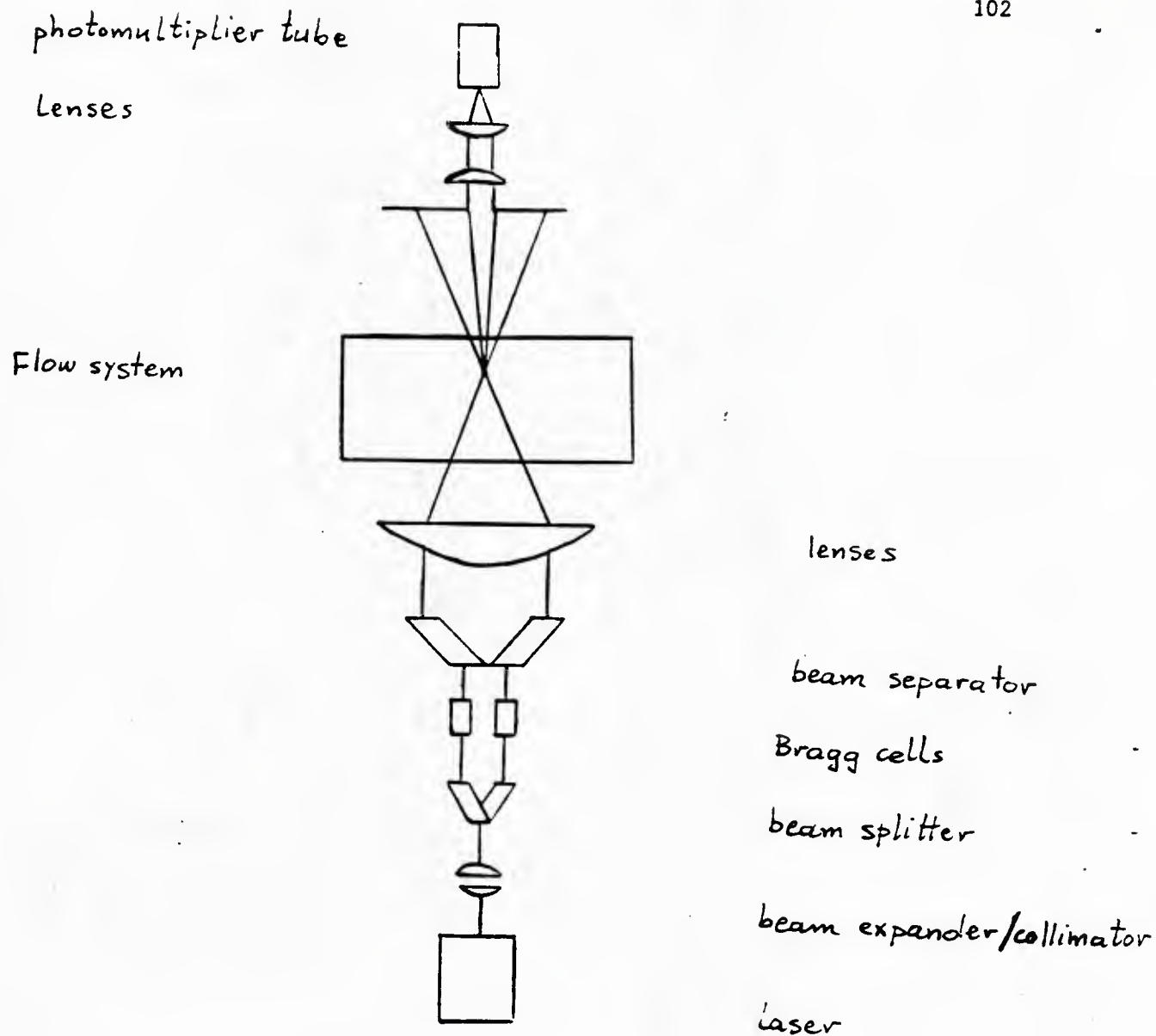
beam expander/collimator

laser

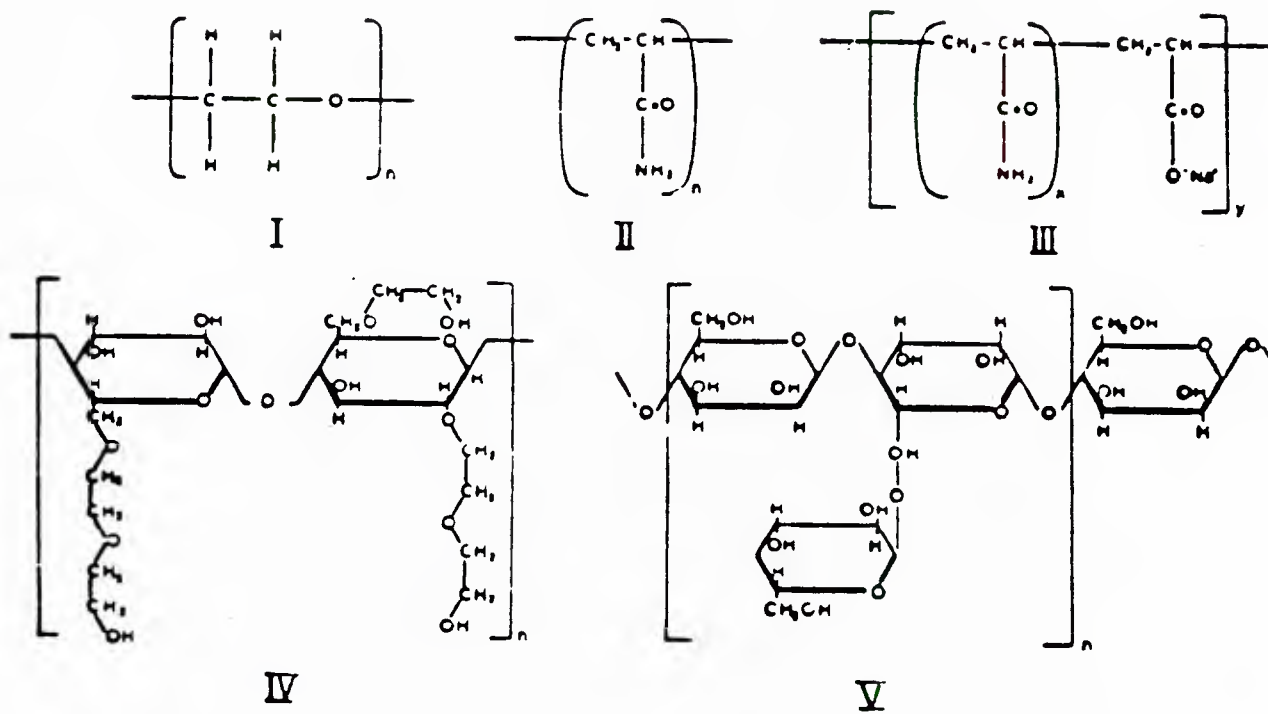**Figure 16:**

Optical arrangement for the LDA studies.

Table 1:

Molecular structure of some typical drag reducing polymers.

I: PEO, II: Nonionic PAM, III: Anionic PAM, IV: HEC, V: Guar gum.

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